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DEVELOPMENT OF A HAZARDOUS
VAPOR DETECTION SYSTEM FOR ADVANCED AIRCRAFT

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Panametrics, Incorporated
Waltham, Massachusetts

TECHNICAL REPORT AFAPL-TR-67-123
October 1967

Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

1968

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DEVELOPMENT OF A HAZARDOUS
VAPOR DETECTION SYSTEM FOR ADVANCED AIRCRAFT

Lester Seiden, Orlando Cucchiara and Philip Goodman


FOREWORD

This report was prepared by Panametrics, Inc., Waltham, Massachusetts, on Air Force Contract AF 33(615)-3646, "Development of a Hazardous Vapor Detection System for Advanced Aircraft." The contract was initiated under Project No. 6075, Task No. 607508. The work was administered under the direction of Fuels, Lubrication, and Hazards Branch, Support Technology Division, Air Force Aero Propulsion Laboratory, Research and Technology Division. Mr. Jon R. Manheim and Mr. Robert E. Cretcher served as project engineers for the Laboratory.

The studies presented here were conducted in the period 1 March 1966 through 1 September 1967, by the Chemistry Department of Panametrics, Inc., Dr. Philip Goodman, Director. Mr. Orlando Cucchiara was the principal investigator.

This report was submitted by the authors September 1967.

This technical report has been reviewed and is approved.


Arthur V. Churchill, Chief
Fuels, Lubrication, and Hazards Branch
AF Aero Propulsion Laboratory

ABSTRACT

A program was conducted to evaluate, develop, and construct instrumentation for the detection of hazardous vapors aboard advanced aircraft. Prototype detection systems were constructed both for monitoring JP-6 fuel vapor in aircraft compartments and for monitoring oxygen in the ullage space of fuel tanks. These systems will be further evaluated in flight tests.

Detection of both species is accomplished by the use of a catalyst-coated thermistor sensor. Catalytic oxidation occurring at the catalyst surface liberates heat, which is sensed by the thermistor.

The JP-6 sensor consists of a simple probe which can be mounted directly in the space to be monitored. No sampling system is required.

The oxygen sensor is more complicated, necessitating flow connections to an external pump and gas supplies.

The instruments developed meet almost all of the desired goals. In a few instances, flexibility for installation in a variety of situations and locations was retained at the sacrifice of some performance characteristics. Methods for achieving desired goals in specific installations and operating modes are indicated and are relatively simple.

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SECTION I

INTRODUCTION

The continuing progress made in the development of advanced air-breathing, hydrocarbon-fueled aircraft has brought with it ever increasing difficulties in coping with fires and explosions. Leakage of combustible fuel or its vapors into various compartments of an advanced aircraft can rapidly lead to explosive fuel-air mixtures. Thus the reliable and rapid detection of low fuel vapor concentrations in potentially hazardous locations within the airframe is of extreme importance.

In addition to the leakage of combustible fuel vapors, there also exists a possible hazard due to the presence of oxygen in the ullage space of the fuel tanks. The fuel temperature in such aircraft is often high enough to create large fuel vapor concentrations above the liquid. In such a situation, the presence of oxygen in any appreciable quantity could present an extremely dangerous situation. This oxygen could arise from at least three sources: (a) outgassing of the fuel under high temperature-low pressure conditions; (b) "breathing" of the fuel tanks during descent of the aircraft; (c) leakage.

It is the purpose of this program to select appropriate state-of-the-art techniques for the detection of both JP-6 vapors and oxygen in advanced aircraft, to construct prototype instruments based on this selection, and to evaluate these instruments under simulated and actual flight conditions.

The state-of-the-art techniques studied included a radiochemical exchange technique using Kryptonates[®], an aluminum oxide hygrometer technique, and a catalytic combustion technique using thermistors. The Kryptonate technique proved to be satisfactory for the detection of hydrocarbon fuels; however, a suitable Kryptonate sensor for the detection of oxygen could not be developed in the allotted time period. The hygrometer technique proved to be suitable for detecting both gases at normal ambient temperatures; however, the aluminum oxide sensor could not be designed to withstand the high environmental temperatures expected for Mach 3 type aircraft.

Catalytic thermal detection was the technique ultimately chosen for both the JP-6 and the O₂ sensors. Instruments based on this technique were developed, constructed and tested in the laboratory. The instruments were found to meet almost all of the desired program goals. The work performed on this subject comprises the main body of the report. The other techniques (Kryptonates and the aluminum oxide hygrometer) are described in the appendix.

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SECTION II

TECHNICAL DISCUSSION

The assumed physical and operational parameters and design requirements for detecting hydrocarbon fuel vapors and oxygen aboard Mach 3 type aircraft were established. These criteria, presented below, served as the target requirements for the instruments developed and discussed in this report.

JP-6 Sensing Device

- a. Temperature - operate continuously from -65° to 650°F .
- b. Sensitivity - capable of detecting fuel vapors from the LEL down to 10% of the LEL or less.
- c. Response Time - 5 seconds at 10% of the LEL
1 second at the LEL.
- d. Recovery Time - no more than 30 seconds.
- e. Selectivity - insensitive to nonexplosive vapors likely to be encountered.

Oxygen Sensing Device

- a. Temperature - operate continuously from -65° to 550°F .
- b. Sensitivity - detect O_2 , in the presence of fuel vapors and nitrogen, at concentrations from 0 to 40% (volume).
- c. Response Time - 5 seconds at 0.5% O_2
1 second at 40% O_2 .
- d. Recovery Time - no more than 30 seconds.
- e. Selectivity - insensitive to other gases and vapors likely to be encountered.
- f. Not adversely affected by exposure to or submersion in liquid fuel.

Complete Systems

- a. Response Time - no more than one second longer than times given above.
- b. Size, Weight and Power - minimum.

- c. Operation - capable of continuous operation; built-in system integrity test capability; both set-point alarm and continuous recording capability (alarm self-canceling).
- d. Installation and Maintenance - simple in concept; highly reliable; easily maintained.

The technique which appeared to most nearly fulfill the above requirements, viz., catalytic combustion, is discussed below. This technique was selected on its ability to withstand the environmental conditions and still provide the necessary sensitivities, response times and other requirements for both JP-6 and oxygen detection. The other techniques investigated are discussed in the appendix.

A. Operating Principle

The principle of operation of the catalytic thermal detection technique is quite straightforward. It has long been observed that certain solid materials catalyze (i. e., increase the rate of) gas-phase reactions which, in the absence of these materials, would proceed at extremely slow rates. Without going into the detailed mechanisms of such phenomena, one may say in general that such catalysts usually exert their effect by means of a selective adsorption process in which molecules of one or more of the gaseous species are held at particular sites on the catalytic surface in configurations (either steric or electronic) which make them highly susceptible to reaction.

If such a reaction is exothermic, then heat will be liberated at the reaction site in proportion to the rate at which the reaction is taking place. If one can measure this liberated heat in some way, then it becomes possible to estimate the relative rate of the reaction. It often happens, when one reactant is present in excess, that this rate is directly proportional to the gas-phase concentration of the other.

Considering gaseous hydrocarbon-oxygen mixtures we find that, in the absence of very high temperatures or of an initiation process, the oxidation rate of the hydrocarbon is usually quite low. If, however, this reaction could be made to occur at a catalytic surface, a sizable amount of heat would be liberated. Even seemingly very dilute hydrocarbon-oxygen mixtures contain surprisingly large amounts of available heat energy. If even a small fraction of this heat could be released to a thermal detector in an appropriate manner, there would be little problem in obtaining very high sensitivities.

For example, let us consider a small parcel of air (1 liter) at standard temperature and pressure, containing JP-6 vapor at a concentration of 0.01% by volume (well below the LEL). Assuming an "average" molecular weight for JP-6 of about 150, one can calculate that there are 6×10^{-4} grams of hydrocarbon in this parcel. As the heat of combustion of JP-6 is about 10^4 cal/gm, there are approximately 6 calories of thermochemical energy

available in this small volume of gas. When one realizes that this is enough energy to raise the temperature of the gas by about 24°C , it is clear that if even a small fraction of this energy could be tapped, a very sensitive detection technique would result.

One may thus envision a detector which could consist of either one of two simple configurations:

- a. A cell packed with catalytic material through which the test gas is passed. Temperature sensors would monitor the gas temperature differential between the inlet and outlet.
- b. A temperature sensor imbedded in a thin layer of catalyst material. The sensor would detect the temperature rise of the catalyst.

Because of considerations involving the necessary response times and the varying environmental temperatures and pressures, it was decided to proceed along the latter course.

"Platinum black," a very finely divided form of platinum metal, is well known as a catalyst for oxidation reactions of this type. This was therefore the prime candidate for use as the catalyst material in the detector.

A thermistor device was chosen as the means for measurement of the catalyst temperature rise. Thermistors consist of mixtures, primarily of metal oxide powders, which have been sintered together into various configurations. These materials typically have a relatively large negative temperature coefficient of electrical resistance, varying by several percent for a change of 1°C . They are available in many configurations, ranging from large (1") discs to small (.005") beads. Figure 1 shows a typical thermistor resistance vs temperature characteristic curve.

The thermistors' large temperature coefficients allow extremely sensitive measurements of small temperature differentials. The simplest method for doing this is an ordinary Wheatstone Bridge circuit, as shown in Figure 2, where small changes in thermistor resistance are readily detected.

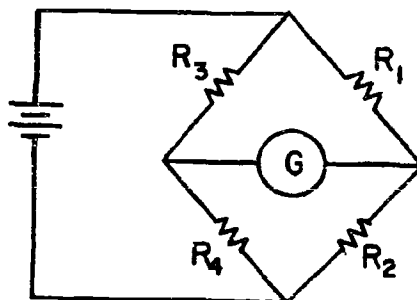


Figure 2. Simple Wheatstone Bridge Circuit

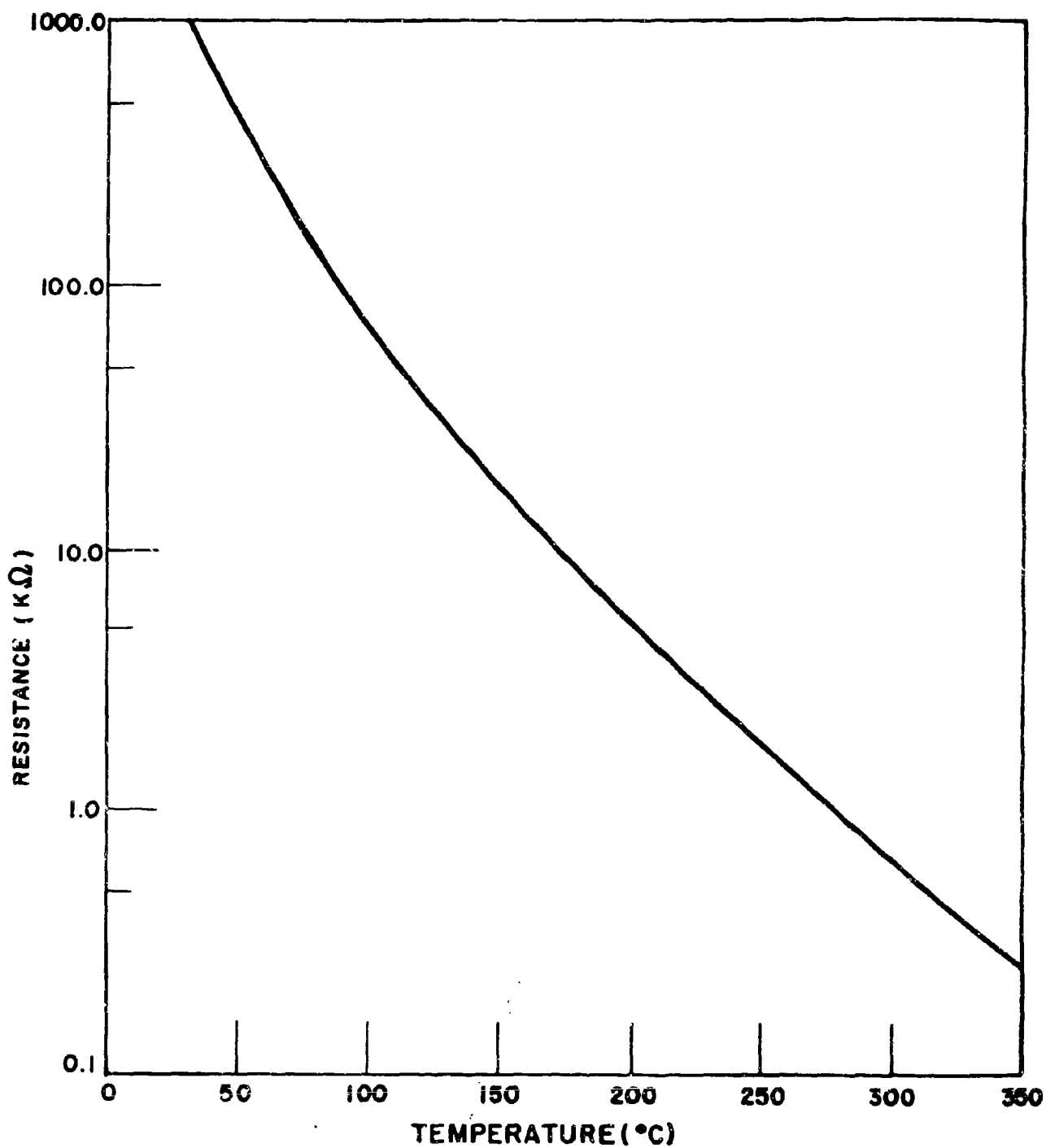


Figure 1. Typical Thermistor "R" vs "T" Characteristic (Fenwal GA61M11)

The bridge is "balanced" when $\frac{R_1}{R_2} = \frac{R_3}{R_4}$. Under these conditions,

$V_1 = V_2$ and no current flows through the galvanometer. If, however, R_1 changes slightly, and if $\Delta R_1 \ll R_1 + R_2$, then the galvanometer current will be proportional to this change.

If R_1 is a thermistor, coated with a thin layer of catalyst, then any increase in its temperature (due to a reaction occurring on the catalyst surface) will be reflected by a corresponding galvanometer current. To negate the effect of changes in ambient temperature, one may substitute a similar, uncoated thermistor for R_3 .

Initially, it would appear that this technique may be applicable as a hazardous vapor detector in both the desired contexts, i. e., as a JP-6 detector in aircraft compartments (where fuel vapor would constitute a hazard), and as an oxygen detector in fuel tank ullage spaces (where oxygen would be a hazard). Certainly in the former application, where JP-6 levels of fractions of one percent by volume in air are to be measured, the oxygen is present in vast excess, and the reaction rate should be controlled by the JP-6 concentration. In the fuel tank, on the other hand, it is expected that in many situations the JP-6 vapor would be in excess, and that the oxygen concentration would thus be the determining factor. However, as will be seen below, although the use of the thermistor sensor as a JP-6 detector is quite straightforward, its use as an oxygen detector is attended by several complicating factors.

B. Investigation and Results

1. Establishment of Gas Mixtures

Similar techniques and apparatus were involved in studying the use of the thermistor sensors for both JP-6 and oxygen detection.

Most of the test gas mixtures were generated in a flowing system by successively adding flows from gas cylinders of known composition. Figure 3 depicts such a system in its most general form. (Usually, not all the connections shown were necessary.) The final gas compositions were calculated from the flowmeter readings.

Two separate streams were established, one (on the left) being the reference stream (i. e., air only, nitrogen + isobutane only, etc.). The other stream was identical to the reference stream, but also contained the substance to be detected (i. e., JP-6 or O_2). After establishing a "zero" reading with the reference stream, the Teflon valve was rotated to substitute the test stream. By keeping both streams flowing at all times, and locating the Teflon valve as close to the sensor as possible, it was found

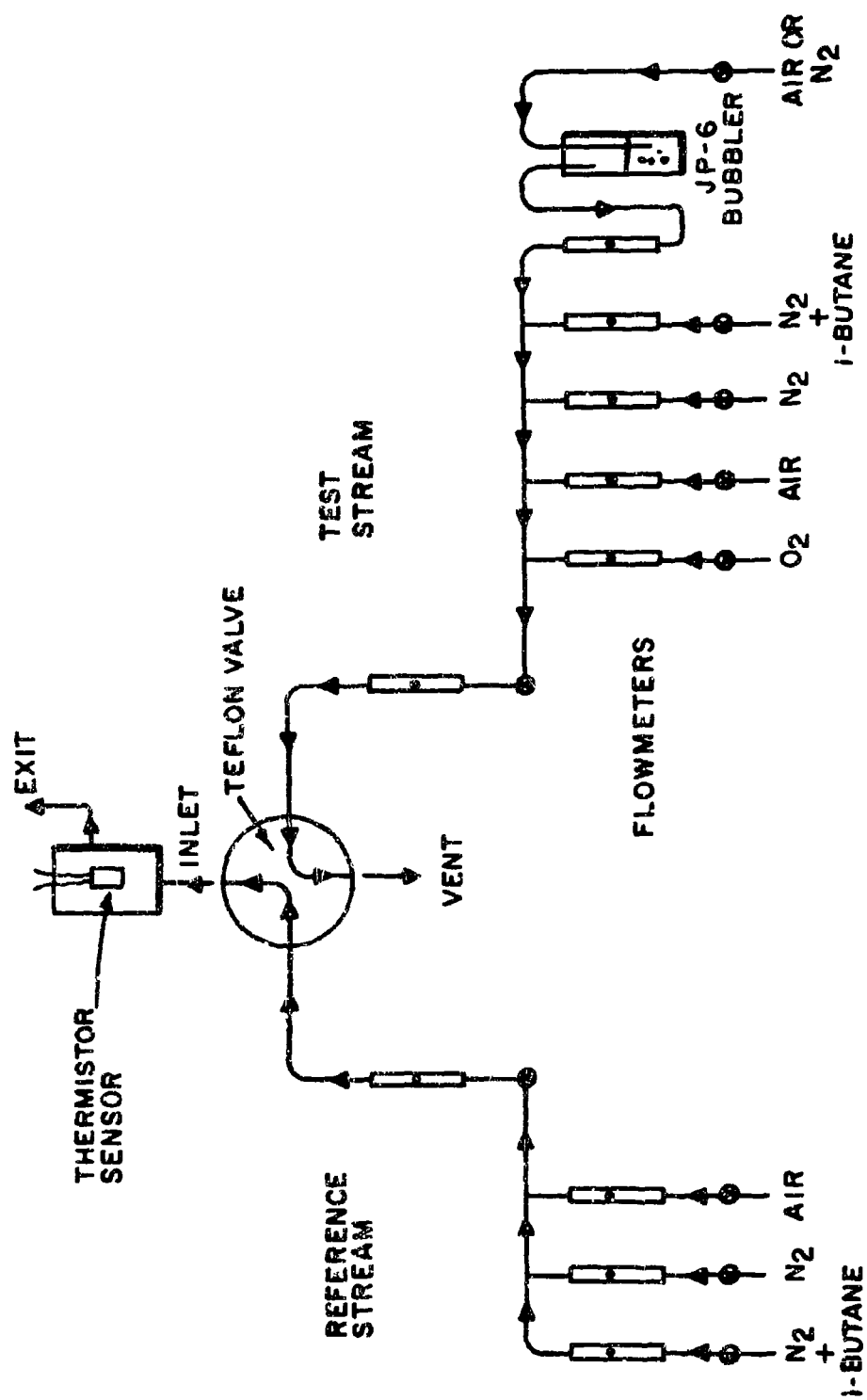


Figure 3. Gas Mixing Manifold

that much more rapid response times were obtained than in flow systems where reference and test gas streams were alternately passed through a single flow line. The longer response times associated with the latter were believed to be due to slow absorption and desorption of vapors on the walls of the tubing, making it difficult to achieve a true "step-change" in gas composition when using a single flow line. Response times of about one second were readily obtained with the flow system shown.

It will be noted that JP-6 was supplied by a bubbler arrangement from which saturated JP-6 vapor was obtained. Unfortunately, because of its variable composition, it is not possible to assume a fixed vapor pressure for this material. It is possible to determine experimentally the concentration by weight of JP-6 in the gas issuing from the bubbler, but because of its variable molecular weight, the volume percentage can only be estimated. As it is a mixture of hydrocarbons, even the weight percentage will tend to vary with time as the JP-6 slowly fractionates, the lower-boiling components being vaporized first. Thus, it was found that fresh samples always yielded higher signals than those which had been in the bubbler for several days. As it was not deemed practical to make continual determinations of the JP-6 concentration (the process being quite time-consuming) it was decided to assume a standard value of 0.6% (wt) at room temperature, based on determinations done at the beginning of these studies, and to put fresh JP-6 in the bubbler every few days. If one assigns an "average" molecular weight of 150 to JP-6, then 0.6% by weight corresponds to 0.11% by volume.

2. JP-6 Detection

a. Operating Temperature

The first experiments were carried out with the simple circuit shown in Figure 4. A small glass-coated bead thermistor (0.040" diameter), coated with a film of platinum black powder, was suspended in a flowing air stream containing no JP-6 vapor.

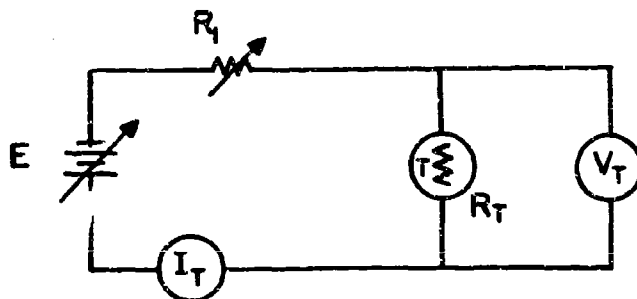


Figure 4. Thermistor Resistance Measurement

By varying E and R_1 enough current could be passed through the thermistor (R_T) to heat it resistively to various temperatures. At each point, by measuring the current and voltage as shown, both the thermistor resistance, $R_T = \frac{V_T}{I_T}$, and the electrical power, $W_T = V_T I_T$, being dissipated in it could be calculated. By reference to a standard chart of R_T vs temperature, the thermistor temperature could be obtained. Thus, the power necessary to keep the thermistor at various temperatures could be found.

The same procedure was then carried out with JP-6 vapors present in the flowing air stream. This time, of course, in addition to the electrical energy being put into the thermistor, chemical energy as well was being supplied by the reaction occurring at its surface. Therefore, with the same settings of E and R_1 , the thermistor would come to a higher temperature than before. Again, this new temperature could be calculated from the R_T vs T chart, and $R_T = \frac{V_T}{I_T}$. Thus, one could obtain: (a) the initial thermistor temperature, (b) the temperature rise due to JP-6 vapor, and (c) the chemical power liberated by the oxidation reaction.

Although these experiments were relatively crude, one significant feature emerged; the catalytic reaction appeared to have a "threshold temperature," below which the rate is quite low. This is illustrated in Figure 5, which shows the net chemical power delivered to the coated thermistor as a function of its initial temperature. Note that below a thermistor temperature of 160°C - 180°C , the energy release rate is practically zero.

As the reaction appeared to be somewhat temperature-sensitive, even in the "plateau" region above 240°C , and as the temperature rise experienced by the thermistor was appreciable in many cases, it was decided to take further data in such a manner that the sensing thermistor would be at constant temperature, both in the absence and presence of JP-6 vapors. This was accomplished by the test circuit shown in Figure 6.

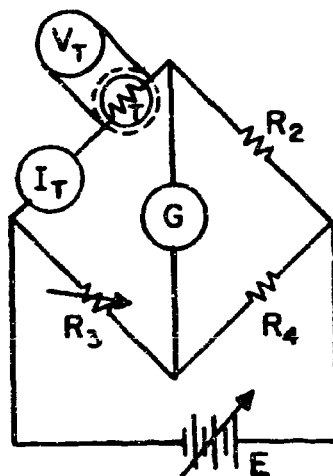


Figure 6. Constant Temperature Bridge

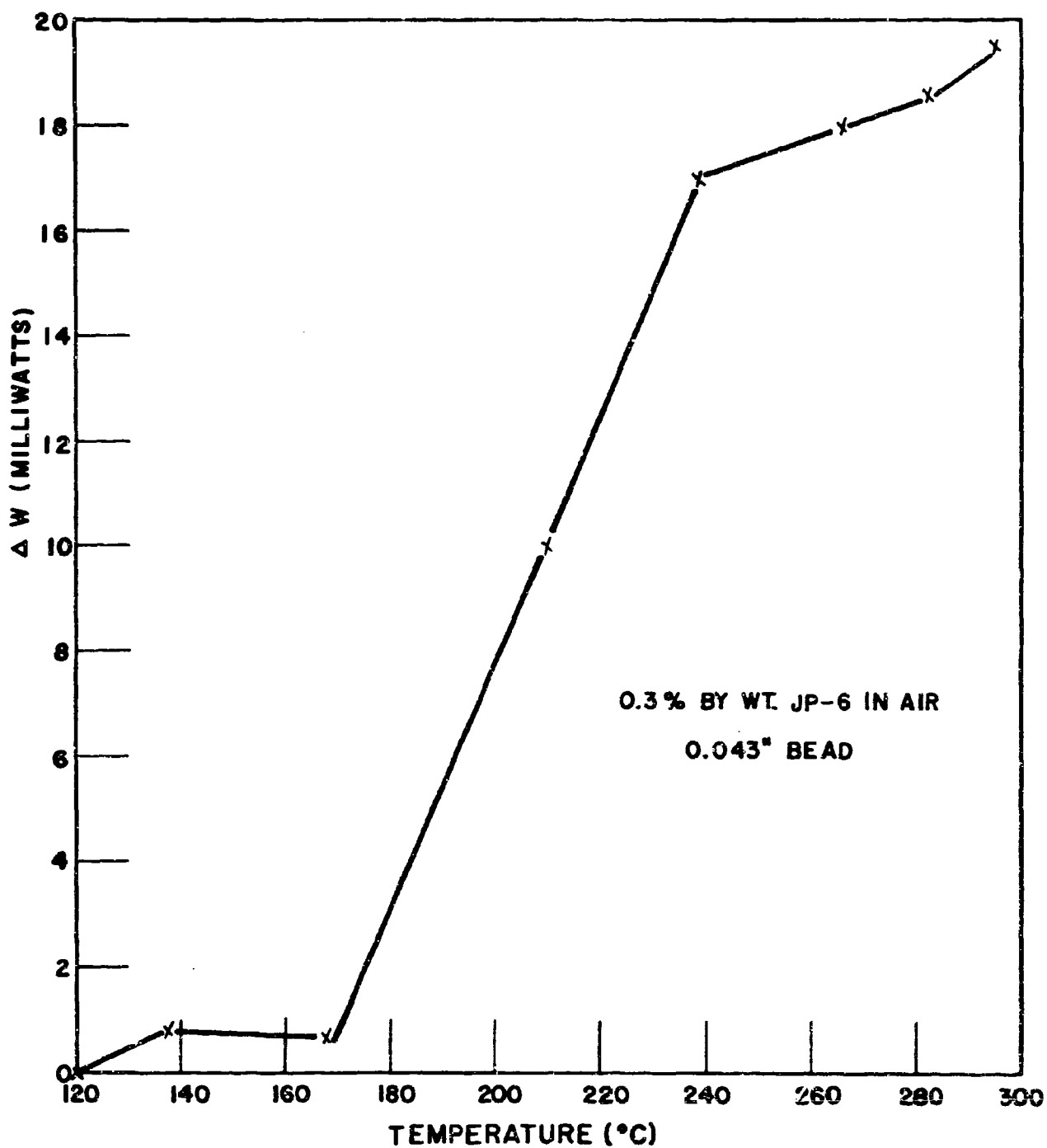


Figure 5. Energy Release vs Temperature: JP-6 in Air

In this case, as before, the catalyst-coated thermistor was first heated electrically to the desired temperature in the absence of JP-6 vapors. At this point, the bridge was put into balance by setting R_3 so that the galvanometer was "nulled." The voltmeter and ammeter readings were then taken, from which the electrical power being dissipated in the thermistor could be calculated. The thermistor was then exposed to JP-6 vapor. As its temperature rose, the corresponding decrease in its resistance caused the bridge to go out of balance. The bridge supply voltage, E , was then decreased, (thus decreasing the electrical heating) until the bridge was again in balance. When this condition was achieved, new readings of thermistor voltage and current were made. As bridge balance was maintained both in the presence and absence of JP-6, the thermistor resistance (and thus the thermistor temperature) remained constant. Therefore, the net decrease in electrical power necessary to maintain the thermistor at constant temperature could be equated directly to the chemical power delivered to the thermistor by the catalytic reaction.

Experiments carried out with this circuitry confirmed the previous temperature-dependence data. It was therefore apparent that the sensor must be kept at a temperature of at least 200°C for effective operation. In view of the fact that the expected maximum ambient temperature could be even higher than this, (340°C) it was anticipated that the final instrument would be designed so that the catalytic sensor would always be operated at the highest possible temperature. Ideally, one would desire this temperature to be at least 340°C . However, the thermistors which were available to us were only rated for a maximum temperature of 300°C . Therefore, 300°C was picked for the "standard" operating temperature, at which all further data would be taken.

b. Linearity

Further work amply demonstrated that, within experimental error, there existed a linear relationship between the JP-6 concentration and the rate of energy release at the thermistor surface. Figure 7 illustrates this data. While, as has been previously noted, the absolute JP-6 concentrations are only approximate, the relative concentrations, (obtained by successive dilutions of the saturated stream) are believed to be accurate. Assuming a value of about 150 for the molecular weight of JP-6, then 0.6% by weight corresponds to about 0.1% by volume (1/5 the LEL).

In order to work at higher JP-6 levels, it is necessary to heat the entire apparatus, including the bubbler, the flow lines, and the detector chamber to prevent condensation of JP-6. Several runs were performed with the entire apparatus placed in a large oven, in order to verify that the detector would operate at JP-6 levels up to and above the LEL.

Increasing signals as a function of oven temperatures were obtained

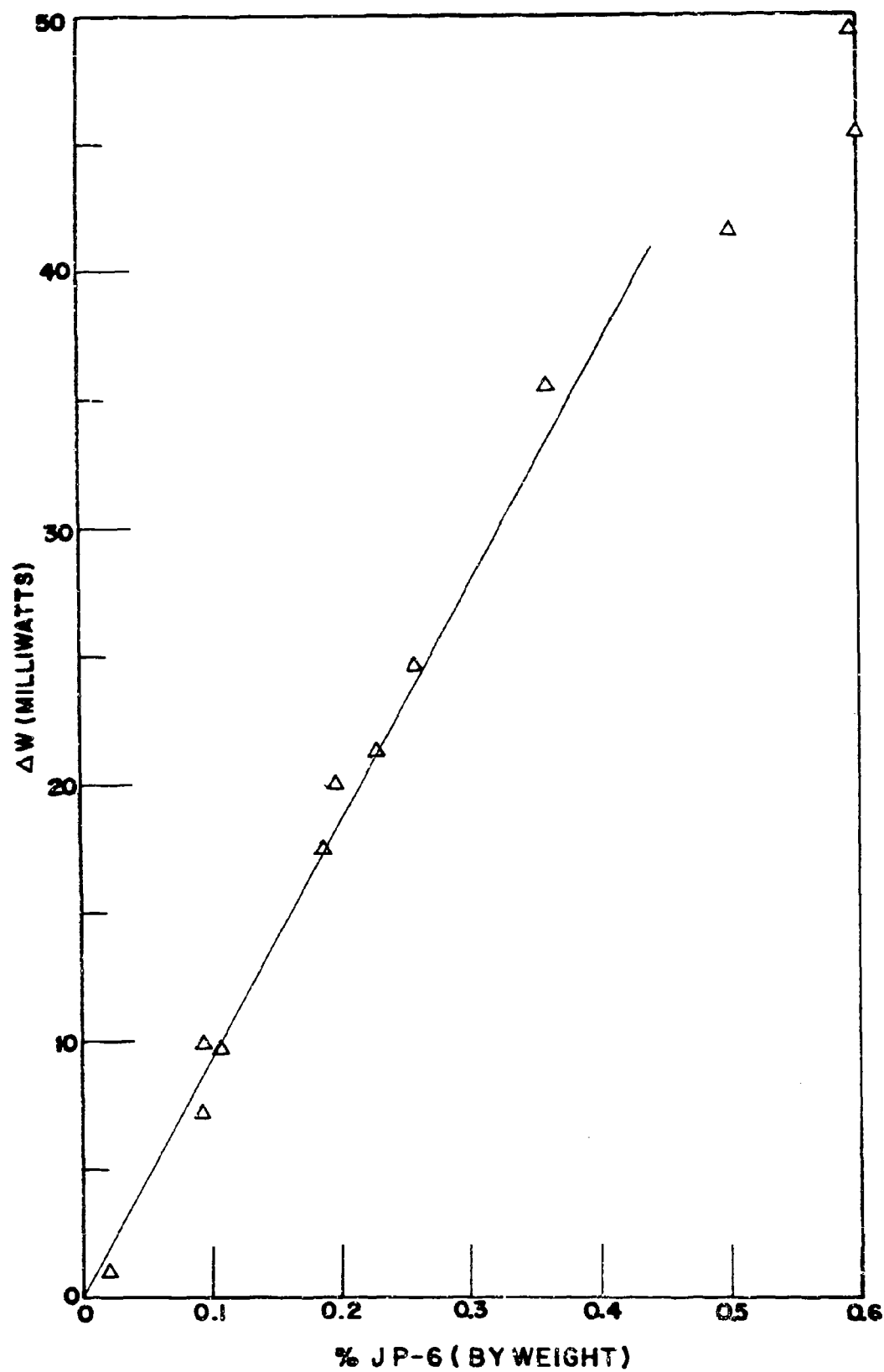


Figure 7. Signal vs JP-6 Concentration in Air

up to 150°F, corresponding to JP-6 levels of approximately 2 to 3 times the LEL. Experimental considerations made it impractical to attempt to measure the actual JP-6 concentrations being generated. However, the magnitudes of the signals obtained at the high temperatures were consistent with the increase in vapor pressure expected at these temperatures. The primary information obtained by this experiment was that the sensor would indeed yield increasing signals up to the highest expected levels of JP-6 in air.

c. Pressure Dependence

To study the pressure dependence of the reaction, a test chamber was constructed (Figure 8) into which JP-6 air mixtures could be leaked at low pressure. In this apparatus, one could compare the relative signals obtained from a fixed JP-6 percentage as a function of total pressure. The procedure used was to generate a flowing JP-6 air stream at atmospheric pressure in the usual manner. A small portion of this mixture was continuously bled into the test chamber through Valve A. By manipulation of Valves A and B, it was possible to hold the chamber at any desired pressure.

Figure 9 illustrates typical data obtained with this apparatus. It was found that the signal from a given JP-6 air mixture was relatively insensitive to pressure over a wide range. This was surprising, in that at 1/2 atmosphere, for example, the absolute JP-6 concentration (i. e., gms/cm³), is only half the original concentration at one atmosphere. One might, therefore, expect the signal to be only half as large.

An explanation for this behavior can be postulated in terms of the catalytic reaction rate being controlled by gas phase diffusion of the reactant molecules to the surface.

Thus as hydrocarbon is depleted by reaction in the immediate vicinity of the catalytic surface, a concentration gradient is established in the gas phase. Under the influence of this gradient, hydrocarbon molecules are continually replenished at the catalyst surface via diffusion inwards from more distant areas of the gas. At equilibrium, a steady-state condition is attained in which the net diffusive current is just equal to the rate of reaction, which of course is proportional to the signal.

Let

- r = distance from center of "bead"
- r_s = radius of spherical catalytic "bead"
- c = hydrocarbon concentration at distance r
- c_∞ = hydrocarbon concentration in bulk gas phase (at $r \approx \infty$)
- c_s = hydrocarbon concentration at catalyst surface.

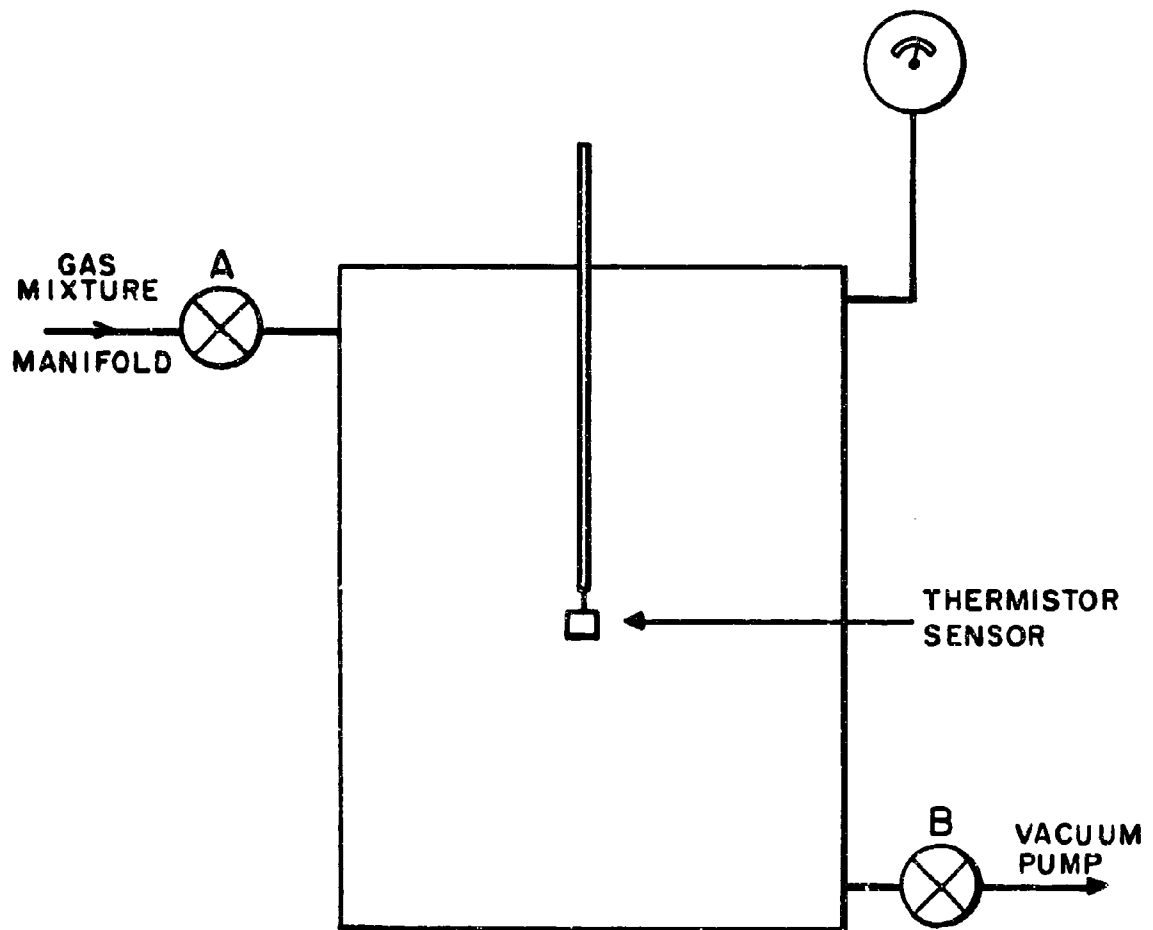


Figure 8. Low Pressure Test Chamber

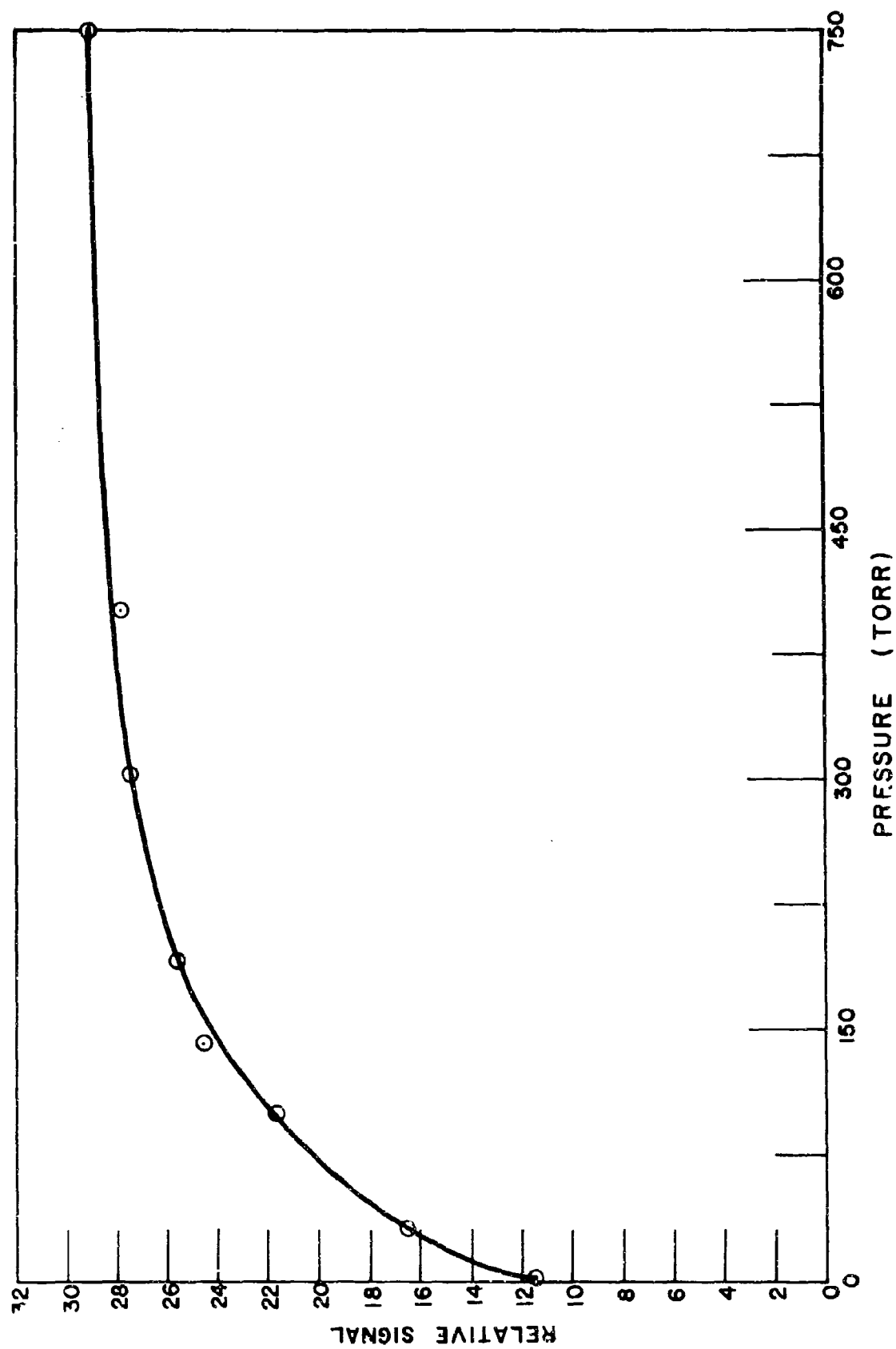


Figure 9. Pressure Dependence of JP-6 Sensor

At any distance, r , the radial diffusive current inward will be:

$$I_r = j_r A_r \quad (1)$$

where j_r = diffusive flux (inward)

A_r = area of spherical shell of radius r .

By Fick's law:

$$j_r = D \frac{dc}{dr} \quad (2)$$

where D = diffusion coefficient for the hydrocarbon in air. Therefore

$$I_r = D \frac{dc}{dr} \cdot 4\pi r^2. \quad (3)$$

Noting that, at steady state, I_r will be a constant equal to the net reaction rate, R , and independent of r , then

$$\frac{dc}{dr} = \frac{R}{4\pi D r^2}. \quad (4)$$

Integrating between the limits $c = c_\infty$ at $r = \infty$, and $c = c_s$ at $r = r_s$,

$$c_\infty - c_s = \frac{R}{4\pi D r_s}. \quad (5)$$

Let us now assume that the reaction rate, R , is proportional to the hydrocarbon concentration at the catalyst surface, c_s , and the surface area of the catalyst

$$R = k c_s \cdot 4\pi r_s^2. \quad (6)$$

Solving the equations (5) and (6),

$$R = \frac{4\pi k D r_s^2 c_\infty}{D + k r_s}. \quad (7)$$

Examining the pressure dependence of this expression, we let

$$D = \frac{D_o}{P}, \quad c_{\infty} = c_{\infty o} P$$

where D_o = diffusion coefficient at $P = 1$ atm
 P = pressure in atmospheres
 $c_{\infty o}$ = concentration of hydrocarbon at $P = 1$ atm
 c_{∞} = concentration of hydrocarbon at pressure P .

Thus,

$$R = \frac{4\pi k D_o r_s^2 c_{\infty o} P}{D_o + k r_s P} \quad (8)$$

Note that at high pressures, when $k r_s P \gg D_o$, R is independent of pressure; as P decreases, however, R ultimately becomes linearly dependent on P . This is qualitatively in agreement with the findings described above. As a rough check on the validity of this treatment, one may substitute into the equation typical values (either known or estimated) for the experimental conditions.

If we consider the case at $P = 1$ atmosphere, and assume that at this pressure, $k r_s \gg D_o$ (as indicated by the small pressure dependence),

$$R = 4\pi D_o r_s c_{\infty o} \quad (9)$$

Setting $r_s \approx 6 \times 10^{-2}$ cm (thermistor bead radius)
 $c_{\infty o} \approx 8 \times 10^{-6}$ g/cm³ (about 0.6% by weight)
 $D_o \approx 0.1$ cm²/sec (estimated for a C_7 hydrocarbon at 250°C),

then $R \approx 7 \times 10^{-7}$ gm/sec.

Using a ΔH of 10^4 calories/gm as the heat of combustion,

Signal $\approx 7 \times 10^{-3}$ cal/sec ≈ 29 milliwatts.

This value is in quite good agreement with the experimentally measured signals (30-50 milliwatts) for these conditions, leading us to believe that the postulated model is reasonably valid.

d. Catalyst Poisoning

Many solid catalysts are known to lose their catalytic activity when exposed to even small quantities of particular gaseous species ("poisons"). This is usually due to the "poison's" ability to disrupt the catalytic reaction mechanism, either by physically blocking the necessary adsorption sites or by permanently changing the nature of the catalytic surface. Platinum catalysts are particularly susceptible to this sort of interference, usually by sulfur and nitrogen compounds. As compounds of this type could easily be present in the ambient atmospheres in which the sensors would have to operate, there was some doubt as to whether the catalyst would be capable of reproducible, long-term operation.

To establish whether this would be a problem, high concentrations (> 90%) of H_2S , SO_2 and NO_2 were passed over a coated thermistor for periods of about five minutes each. None appeared to have any adverse effect on the catalytic activity of the coating. These experiments indicate that poisoning of the catalyst will not be a serious problem.

3. Oxygen Detection

a. General

The use of the coated thermistor probes for sensing oxygen in fuel tanks was investigated using essentially the same apparatus and techniques as for the JP-6 detector. As explained in Section A, it was expected that substantially the same type of sensor could serve to monitor oxygen (in the presence of excess JP-6) as was shown to monitor JP-6 (in the presence of excess oxygen).

Of course, it was clear that under certain of the expected conditions existing in the fuel tank, particularly at low temperatures, an excess of JP-6 vapor would probably not be present. However, it was decided to investigate this technique to define its operational limits, with the expectation that, if this were the only drawback, supplementary means (e.g., heaters, etc.) could be incorporated for obtaining the necessary fuel vapor concentrations.

b. Reaction of O_2 With Isobutane

The first experiments were performed to determine the response of the thermistor probe to various oxygen concentrations in the presence of a simulant hydrocarbon. A simulant was used, rather than JP-6 itself due to the practical difficulties involved in generating high concentrations of JP-6 vapor. Because it was readily available, isobutane was chosen as the simulant hydrocarbon.

Initial results indicated that, at a fixed isobutane concentration, signals were usually obtained which were indeed proportional to the oxygen

concentration. However, a major difficulty arose which had not been foreseen. This was the appearance of a "quenching" phenomenon at high oxygen concentrations. This is illustrated in Figure 10, which shows that as the oxygen concentration was increased the signal increased to a maximum. Past this point, the signal then decreased with increasing oxygen concentration. Furthermore, the oxygen concentration at which quenching occurred was a function of the isobutane concentration. There was also some evidence that it was a function of the particular experimental arrangement (i. e., probe configuration and temperature, chamber geometry, etc.) as well.

Ensuing experiments confirmed the fact that this phenomenon was indeed what it appeared to be, i. e., a decrease in the oxidation rate. (It could have signified, for example, a large increase in rate, with expansion of the reaction zone into a flame front located away from the thermistor surface. This would have the effect, of course, of diminishing the surface reaction.) The oxidation of hydrocarbons results in the formation of water vapor as a major product. Therefore, by monitoring the water vapor concentration in the gas emerging from the sensor chamber, it is possible to determine whether or not oxidation is occurring. An aluminum oxide hygrometer element (described in the Appendix) mounted downstream from the sensor chamber, definitely established that the reaction was truly being quenched, and that no enhanced oxidation was occurring in the gas phase. High water vapor levels were found when the thermistor signal was high, with a marked decrease at the "quench point."

Thus far no detailed explanation of this phenomenon is available. One possibility is that at high oxygen levels, the reaction rate is being limited, not by the oxygen concentration, but by the isobutane concentration. This, however, ought to result in a plateau in the signal vs O_2 curve, and not a decrease as is found. Similarly, an explanation based on the reaction being inhibited by the buildup of excess product species on the catalyst surface does not appear to accord with the ability of the quench point to shift as a function of isobutane concentration. The most likely explanation appears to be one which portrays the quenching as being due to some sort of "blockage" of hydrocarbon absorption on the catalyst by oxygen molecules, the quench point being a function of the relative gas-phase concentrations of isobutane and oxygen and their respective adsorption isotherms.

c. Reaction of O_2 With Other Hydrocarbons

A study was undertaken to establish whether the quenching effect was unique to the isobutane-oxygen reaction or whether it existed with other hydrocarbons as well.

Propane and methane were examined in a similar fashion, with disappointing results. Propane (Figure 11) showed a tendency toward quenching, although the signal maxima were higher and the decreases in signal were not

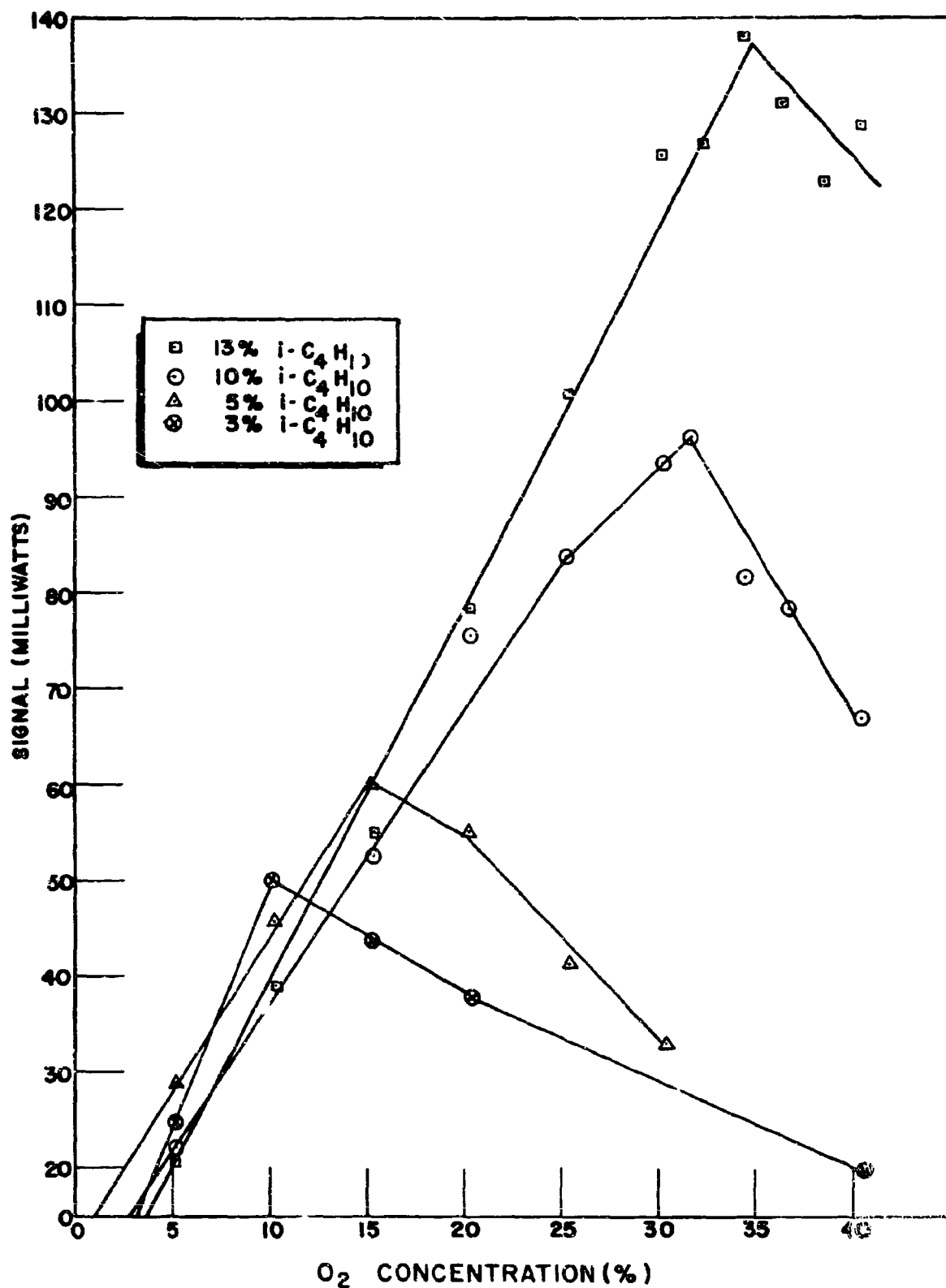


Figure 10. Signal vs O₂ Concentration: Isobutane in N₂

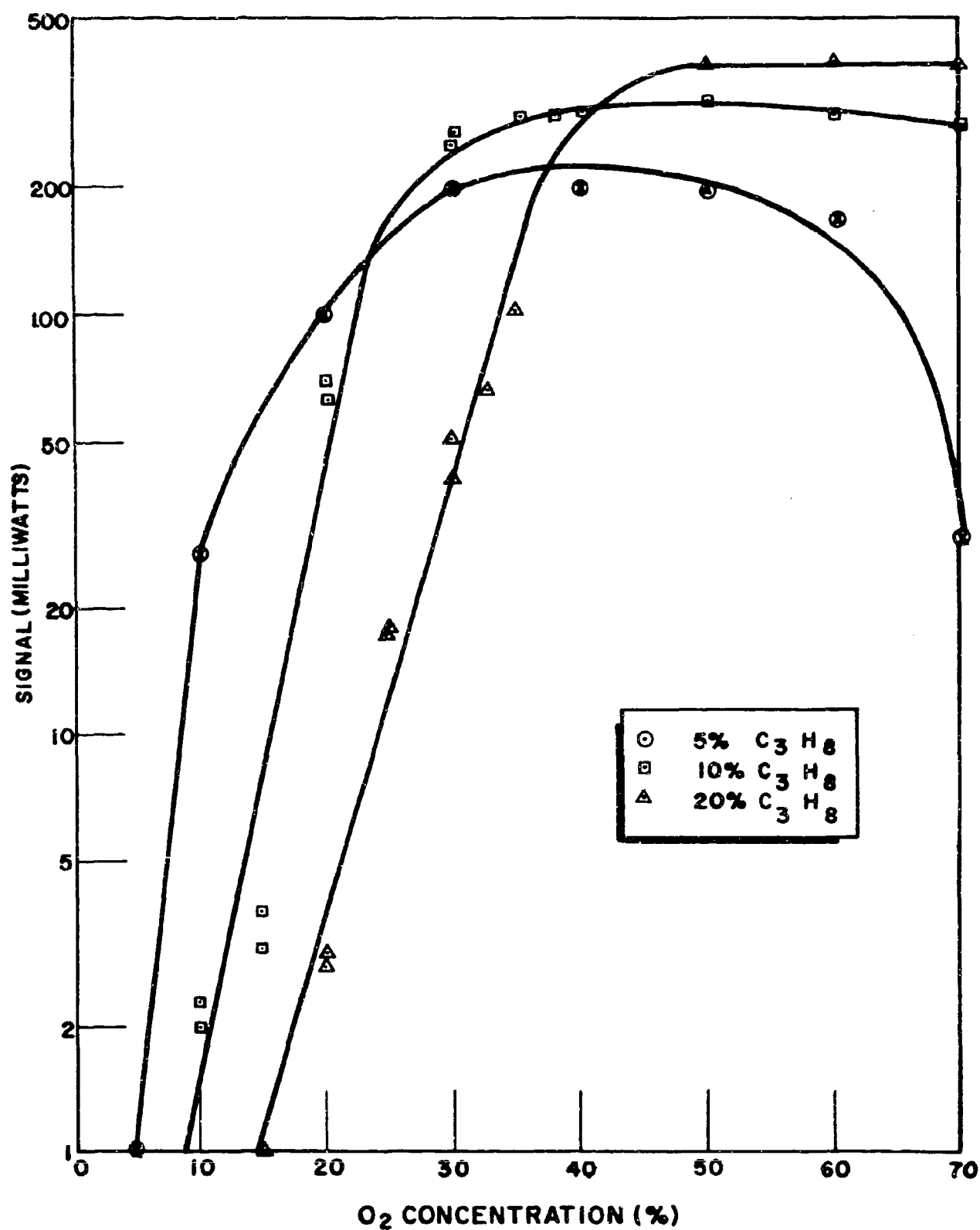


Figure 11. Signal vs O₂ Concentration: Propane in N₂

as marked. However, the "unquenched" signals were not linear with oxygen concentration. Methane, on the other hand, showed extremely poor sensitivity to oxygen. The signals obtained were so low that it was difficult to tell whether or not quenching was taking place.

The varying behaviors of the three simulant hydrocarbons cast doubt on the validity of using any of them to predict the behavior of like concentrations of JP-6.

d. Reaction of O₂ With JP-6

Concurrent with the studies described above, which utilized simulant hydrocarbons, several attempts were made to achieve a means for supplying a high JP-6 vapor pressure to the oxygen detector at all times, even at low ambient temperatures. At this time, it was still assumed that vapors from the JP-6 in the fuel tank would ultimately serve to react with the oxygen at the catalytic surface. (It was expected that the simulant hydrocarbon studies would yield data as to the appropriate JP-6 levels which should be maintained in order for the detector to afford good sensitivity for oxygen.)

Among the possible methods envisioned for accomplishing this purpose were such devices as a heated "wick" of absorbent material, whose lower end would be immersed in the JP-6. Another such device was a small JP-6 "boiler" which would supply a jet of JP-6 vapor in the vicinity of the sensor. Results obtained using these devices in conjunction with the thermistor probe were disappointing, the signals being very erratic and nonreproducible. Even at oxygen levels which were low enough so that quenching (on the basis of the isobutane data) should not take place, abrupt signal decreases were noted.

From indications obtained in these studies, it seemed likely that the erratic behavior of the sensor was due, in part at least, to the high (and at times variable) JP-6 concentrations involved. If this were true, then the concept of monitoring for oxygen by utilizing the excess JP-6 vapor present in the fuel tank would be invalid.

C. Discussion

On the basis of the above results, use of the catalytic thermal detector for measuring JP-6 in air appeared extremely promising. The sensor need consist of nothing more than a simple probe suspended in the space to be monitored, with appropriate electrical connections to the readout circuitry.

At the same time, it was quite clear that the detection of oxygen by means of a similar sensor would by no means be as straightforward as had been expected. It was still felt, however, that in terms of engineering simplicity, it would be highly desirable to use the same type sensor for both JP-6 and oxygen. On the basis of the data at hand, an alternative approach

was taken which, although it promised to be relatively complex, would make use of the same basic principle.

It had been shown that oxygen levels could be monitored by hydrocarbons such as propane and isobutane. Of the hydrocarbons tested, isobutane appeared to yield linear signals as a function of oxygen concentration. At too high an oxygen level "quenching" occurred. However, it was possible to measure oxygen concentrations approaching 40% (the upper limit called for) by using a high enough (~13%) isobutane concentration. It was also clear that too high a JP-6 concentration led to erratic results when measuring oxygen. Therefore it was suggested that

- a) a means be devised for eliminating the high JP-6 concentrations (that might occur in a hot fuel tank) from the gas sample.
- b) then adding a large enough amount of isobutane, allowing the oxygen measurement to be made.

Such a device would, of course, necessitate a flow system such as is schematically illustrated in Figure 12. Gas from the ullage space is first drawn past a cold surface which maintains the JP-6 vapor pressure in the stream at a low value by condensation. Immediately downstream a controlled leak of isobutane is mixed with the gas stream. The oxygen content of the gas is then measured by the thermistor sensor.

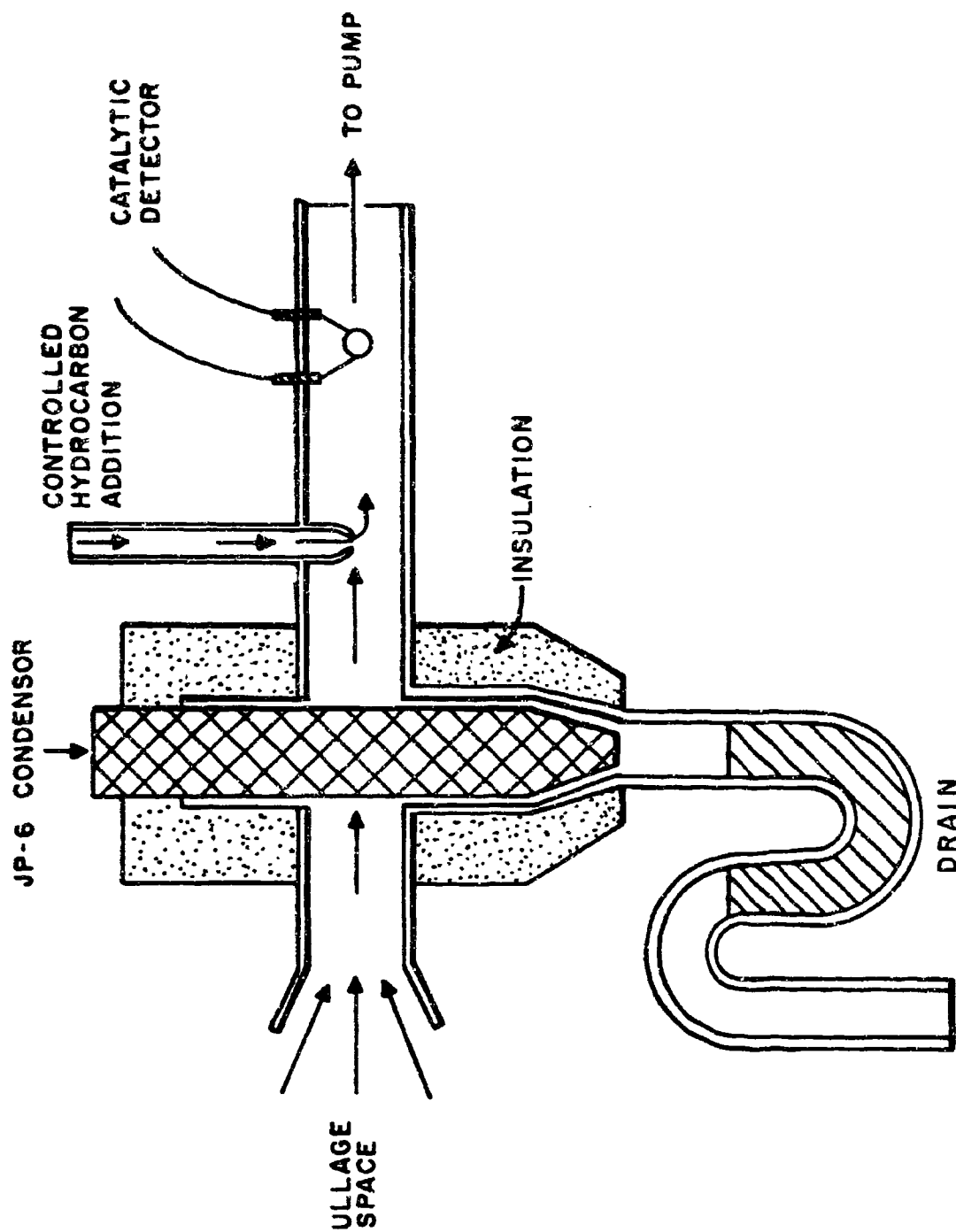


Figure 12. Possible O₂ Detector Configuration

SECTION III

INSTRUMENT DESIGN

The final design for the prototype instruments was determined at a time when the particular aircraft in which flight tests would be performed had not yet been determined. Indeed the installation location was not known. The instruments were therefore designed with the greatest possible flexibility. In certain instances this necessitated design compromises, some of which are discussed in Section V.

A. General Considerations

1. Thermistor Configuration

Most of the laboratory data had been taken with a coated thermistor heated resistively, and suspended by its electrical leads in the gas stream. This configuration is the most sensitive thermally, i. e., with respect to the conversion of the chemical energy release on the coating into a corresponding temperature rise of the thermistor. Another way of stating this is that the "dissipation constant" of the thermistor (milliwatts/°C) is low. As the thermal losses to the surroundings are small (conduction and convection to the gas plus conduction through the very thin leads) most of the energy delivered to the catalytic coating is "seen" by the thermistor, and results in a large temperature change.

The "nulling" circuit, described above (Figure 5), keeps the thermistor temperature constant while retaining the high sensitivity of the low-dissipation physical configuration. In this circuit, the electrical heating power, W , is adjusted to maintain the thermistor temperature at a constant value (by maintaining bridge balance). Hence, the decrease in electrical power, $W_0 - W$, is a measure of the added chemical power.

While useful for laboratory studies, this arrangement has several deficiencies when considered in the context of a final instrument. For example, there is no means of compensation for the effects of varying ambient temperatures and pressures on W_0 , the electrical power necessary to maintain the thermistor at the proper temperature in the absence of reaction. (This is no drawback in the laboratory, where W_0 can be remeasured after each change in ambient conditions.)

An even more serious deficiency is the limited range of signals which can be accepted at higher ambient temperatures. This is because the only way that one can hold the thermistor temperature constant as ambient temperature rises is to decrease the electrical power input. Thus, at an ambient temperature of 25°C, it takes approximately 150 milliwatts to maintain the

thermistor at 300°C . Under these conditions a chemical reaction yielding 50 milliwatts is quite acceptable; to maintain the thermistor at constant temperature, the electrical power input is decreased to 100 milliwatts, and the "signal" is calculated to be $W_0 - W = 150 - 100 = 50$ milliwatts. If, however, the ambient temperature is 275°C , then W_0 is only about 10 milliwatts. Obviously, in this case a chemical power input of 50 milliwatts cannot be compensated even by decreasing the electrical power to zero, and the bridge cannot be rebalanced.

Another undesirable feature of this technique is the method for heating the thermistors to operating temperature. Conversations with thermistor manufacturers indicated that, although the thermistors are rated to withstand an ambient temperature of 300°C , heating them to this temperature resistively is undesirable. This is because the thermistors, being composed of sintered particles, are not necessarily homogeneous on a micro scale, and continued passage of large electrical currents through them might cause resistance changes due to "hot spots," particularly at the thermistor-lead wire interface.

An alternative arrangement was therefore proposed, in which the catalyst-coated thermistor would be heated to the proper temperature indirectly, e.g., by mounting it in a heated block. Separation of the functions of heating the thermistor and sensing its resistance allows the use of a compensated high-sensitivity bridge circuit.

Figure 13 depicts this sort of configuration. It consists of two matched thermistors, mounted in a metal block; one is coated with catalytic material, and the other with inert material. The block is heated electrically to 300°C . In the absence of catalytic combustion, they both assume the block temperature, and the bridge is balanced. If reaction occurs at the catalyst, the liberated heat changes the temperature of the sensing thermistor.

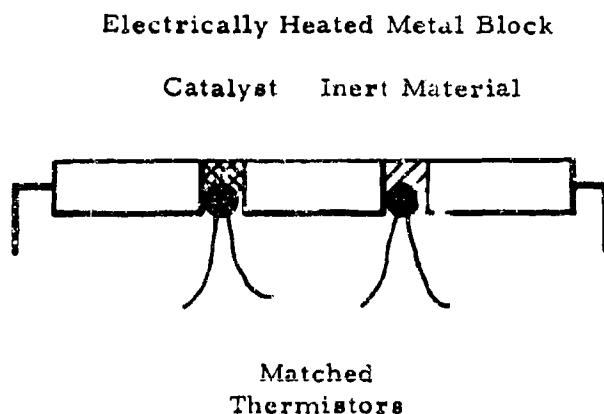


Figure 13. High-Dissipation Configuration

The resulting change in resistance is read as a bridge imbalance signal. Note that in this configuration the thermistor is in good thermal contact with the block resulting in a high dissipation constant. Therefore even very large chemical power inputs will not change the temperature of the coating more than a few degrees. This means that if the block temperature is held constant the reaction will always be occurring at essentially the same temperature. Although the maximum signal will correspond to only a few degrees difference, adequate sensitivity still ought to be available (precision thermistor bridges can readily measure ΔT 's of several millidegrees).

Results with this configuration were very satisfactory. Figure 14 depicts two early approaches which were tried. Emphasis was put on making the sensor as small as possible, while at the same time allowing reasonable ease in assembly.

As an aid in preliminary evaluation of heated-block detectors using this configuration, a dual bridge circuit was constructed which enabled both (a) the detector output signal to be displayed, and (b) the resistance of either thermistor to be individually measured, at any time during the experiments. This circuit is shown in Figure 15. In the "Detector" mode of operation, the thermistor pair serves as two arms of a Wheatstone bridge, which is "nulled" using the Detector Balance potentiometer in the absence of hazardous vapor. When reaction occurs at the coated thermistor, increasing its temperature, the resulting bridge imbalance causes an output signal at the microammeter.

In the "resistance measurement" mode either of the two thermistors can be connected into a separate, equal-arm Wheatstone bridge, whose variable arm is controlled by the thermistor resistance potentiometer. With this control adjusted so as to null the bridge the thermistor resistance, R_T , is read directly from its dial as shown. The circuit shown is for use with thermistors having resistances in the 300-500 Ω region.

The physical configuration finally arrived at for the prototype instruments is shown in Figure 16. It consists of a small cartridge-type heater to which a triangular brass block has been soldered. The block is drilled and countersunk as shown, and selected matched pairs of thermistors are placed in the holes so that they are flush. The thermistors are cemented in place using a mixture of "Saureisen" binder with finely powdered copper. This mixture was chosen so as to withstand high temperatures and yet have as high a thermal conductivity as possible.

2. Temperature Control

In order to maintain the heated block at constant temperature under varying ambient conditions, one must incorporate a means for controlling the heater power. This is accomplished by the use of a third thermistor, also imbedded in the block, to sense any deviations in block temperature from a preset value. This thermistor is connected into a proportional

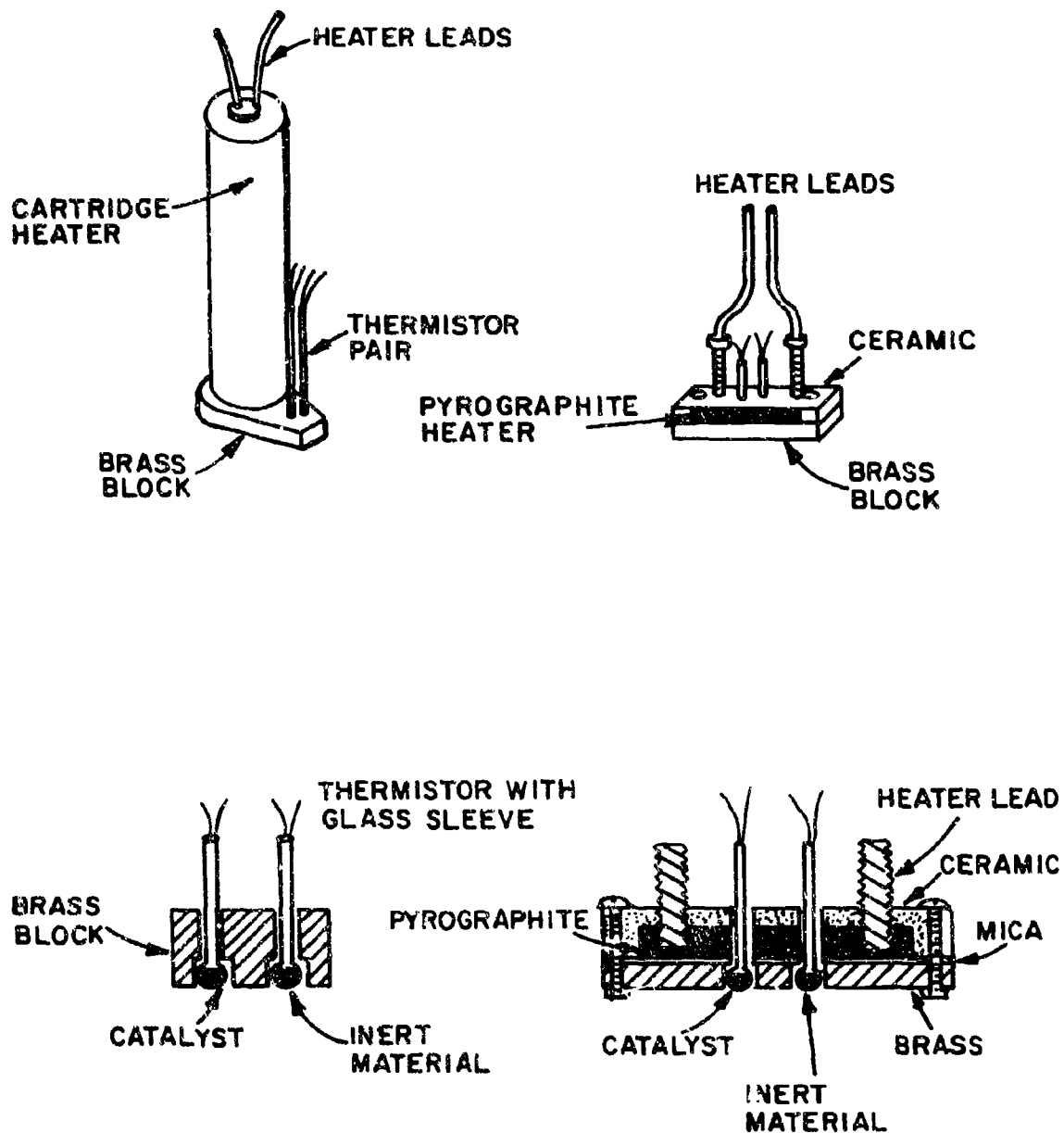


Figure 14. Typical High-Dissipation Mountings

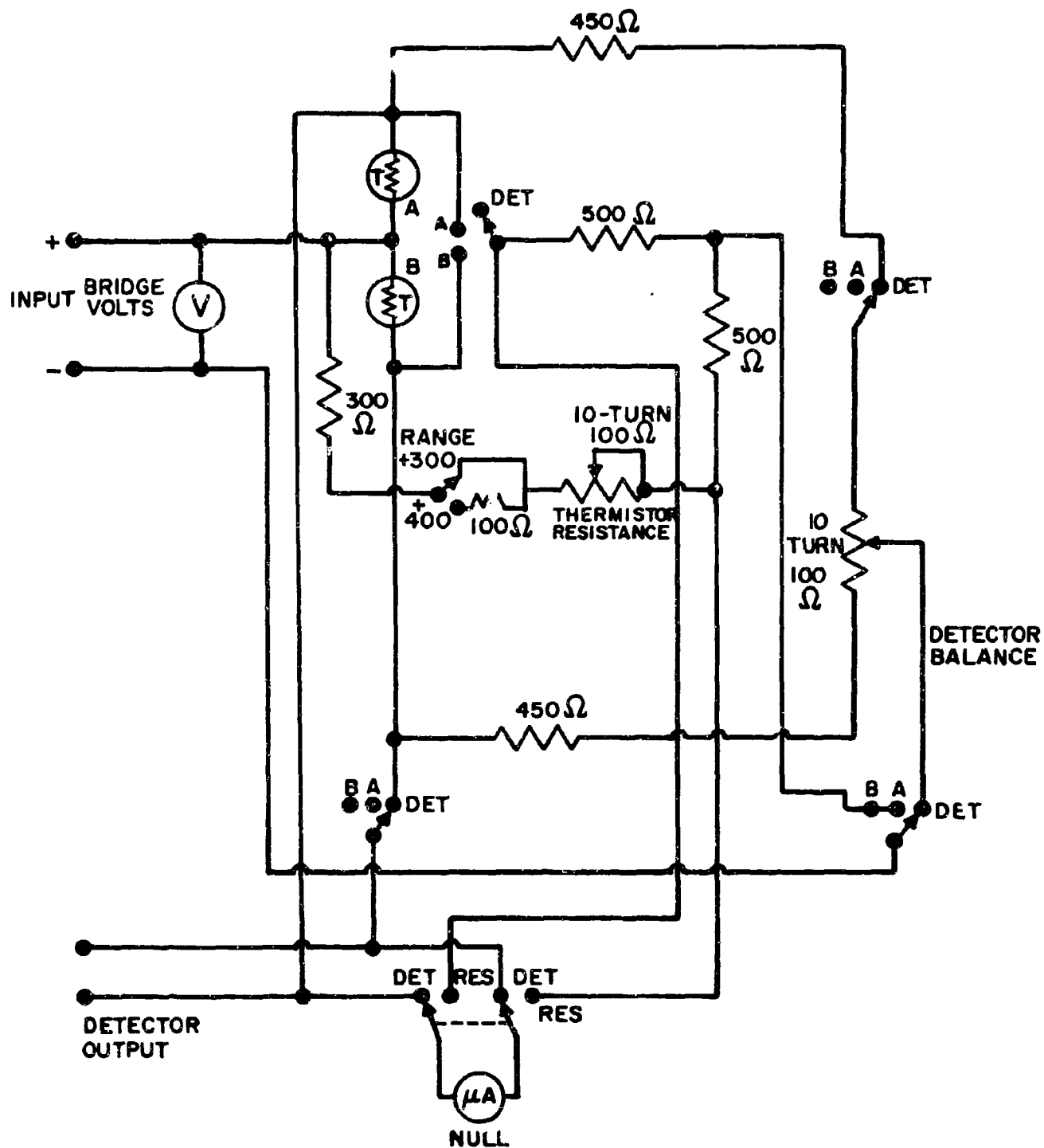


Figure 15. Auxiliary Bridge Circuit

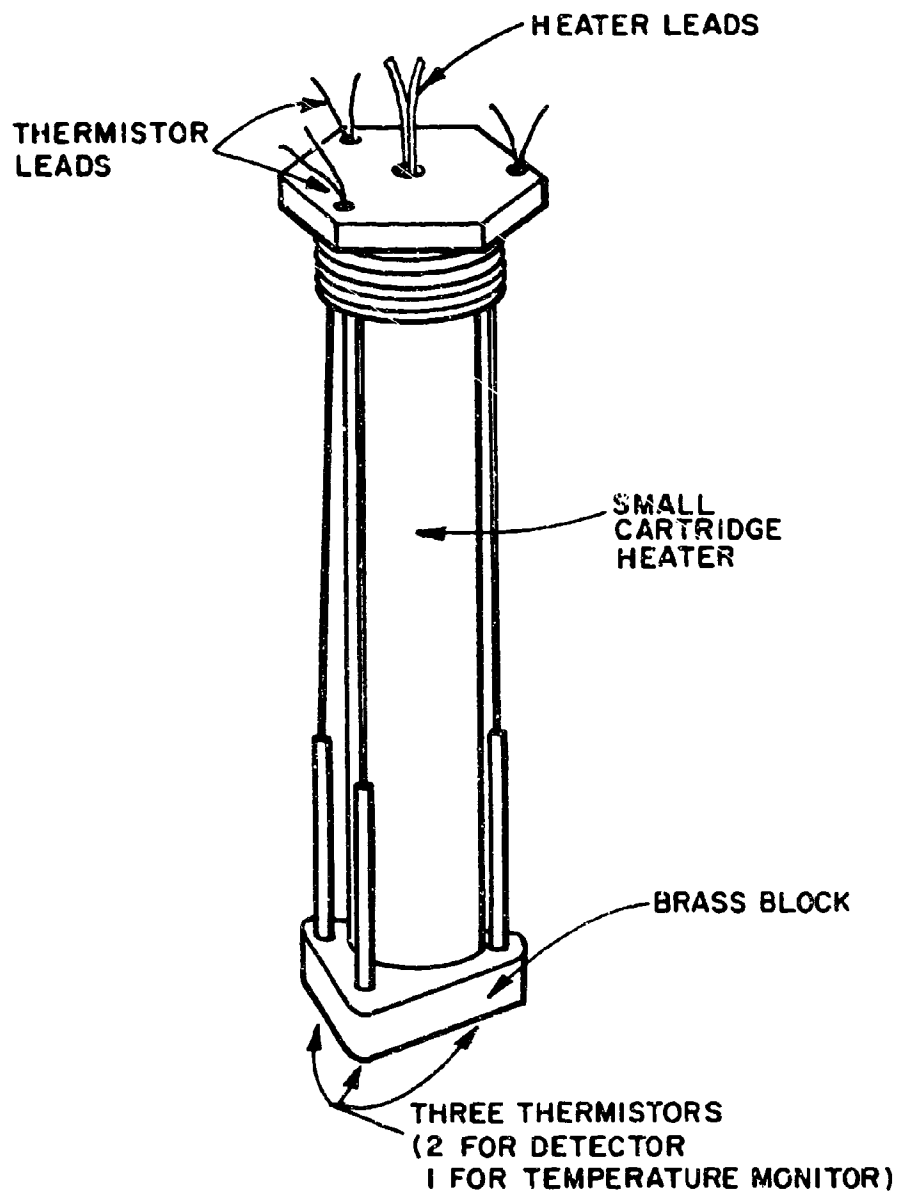


Figure 16. Final Sensor Configuration

controller, which automatically adjusts the heater power to maintain it at a constant resistance (Figure 17). This temperature-monitoring thermistor is mounted in the third hole in the same manner as the matched pair.

3. Thermistor Selection

The thermistors selected for use in the sensors were Fenwal Model GA61M1. These were chosen primarily because of their construction, which is shown in Figure 18. Note that, in addition to the glass coating on the thermistor bead proper, there is a glass sleeve which extends along the lead wires for approximately 1/2 inch.

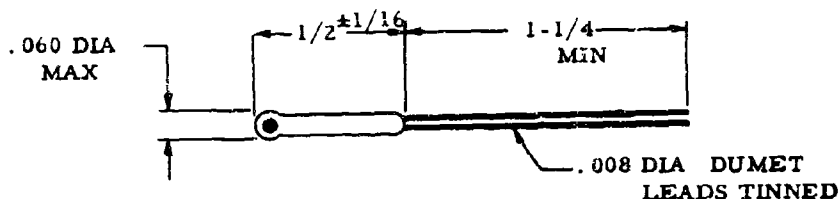


Figure 18. Thermistor Construction

The extra length of insulation allows the thermistors to be emplaced in holes in the metal block conveniently without encountering problems due to the leads touching either each other or the block. These thermistors have a nominal resistance of 1 megohm at room temperature, and about 520 ohms at 300°C. However, these nominal values are useful only as guides, the individual thermistors having possible deviations of up to 20%.

In order to select appropriate thermistor pairs for use in the sensors a batch of 25 were submitted to the manufacturer for precision resistance measurements. Resistance values were obtained at 290°C, 300°C, and 310°C. From the results of these calibrations, as shown in Table I, appropriate matched pairs were selected. It will be seen that the selected pairs matched each other to within 0.5% at the temperatures in question. Note that, as the sensor will always be operating in this region, this is the only temperature range which need concern us as regards matching the thermistor pairs. It should also be noted that, the better the pairs are matched, the less stringent will be the temperature control requirement for the heater block.

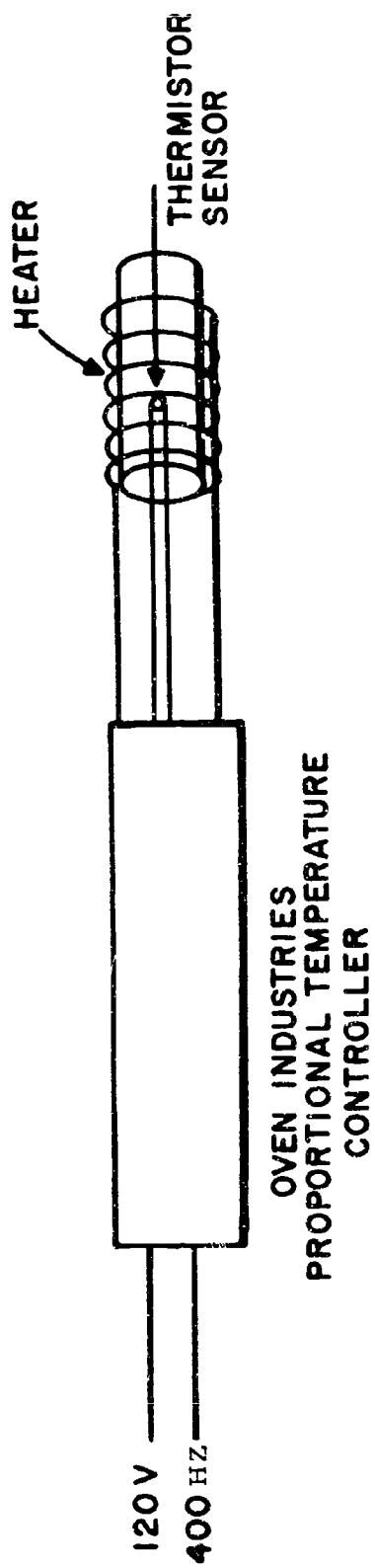


Figure 17. Temperature Controller Circuit

Table I

Resistance Values of Matched Thermistor Pairs

| Pair | Thermistor No. | Resistance, ohms | | |
|------|----------------|------------------|-------|-------|
| | | 290°C | 300°C | 310°C |
| 1 | 17 | 488.3 | 414.5 | 352.5 |
| | 23 | 488.2 | 413.4 | 351.7 |
| 2 | 14 | 498.4 | 422.4 | 359.3 |
| | 12 | 496.9 | 421.9 | 359.8 |
| 3 | 11 | 503.5 | 426.6 | 362.8 |
| | 21 | 502.9 | 425.8 | 362.1 |
| 4 | 15 | 506.2 | 429.0 | 364.6 |
| | 25 | 506.3 | 429.3 | 364.9 |
| 5 | 4 | 508.0 | 430.9 | 367.5 |
| | 22 | 507.6 | 430.4 | 365.6 |
| 6 | 3 | 542.1 | 459.7 | 391.2 |
| | 7 | 541.1 | 458.8 | 390.4 |

4. Catalyst Coating

A difficult practical problem has been that of ensuring good adherence of the catalyst to the thermistor surface. In the earlier laboratory studies, the catalytic coatings were produced by simply making up a slurry of platinum black powder in water, and painting this mixture onto the thermistor. The resultant coatings, after drying, were extremely delicate as there was essentially no adherence between the metal powder and the glass surface of the thermistor. The sensors made in this fashion continuously lost their coatings, as the powder would shake off in the course of normal handling. Such an arrangement was obviously unsuitable for a flight instrument, and various alternative methods were attempted.

Although it was possible to get extremely good adherence by mixing the platinum powder with "cements" of various types, it was found that these usually defeated the purpose by covering the platinum black particles, thus preventing access of the gas to the catalyst.

In situ formation of metallic platinum on the thermistor surface was also attempted. This was accomplished by painting the bead with a solution of platinum chloride, followed by either reduction with hydrogen or high temperature decomposition. This method yielded thin metallic platinum films which, while adherent, were much less active, catalytically, than the powder.

The catalyst coating ultimately found to be most satisfactory, both in terms of adherence and catalytic activity, was a mixture of equal parts platinum black and silica gel "G". The latter is a special silica gel formulation, for use in thin layer chromatography, which contains a small amount (5%) of calcium sulfate binder. A thick water slurry is made of the platinum black-silica gel mixture and then "painted" onto the thermistor. The corresponding "inert" coating on the compensating thermistor, is made from the silica gel alone. After air-drying, a reasonably adherent coating is produced. Although this coating will not shake off, it can be very easily rubbed off. Therefore, reasonable care in handling should be exercised. In the assembled sensor, the thermistors are protected by a metal shield which surrounds the heater assembly.

5. Bridge Circuit

The Wheatstone bridge circuit used in the prototype instrument is shown in Figure 19. The regulated power supply accepts a 115 volt 400 Hz input, yielding a dc output of 10 volts. The instrument sensitivity is determined by the portion of this voltage which is applied to the bridge; this is adjustable by means of the potentiometer R6. The bridge output signal is displayed on a 0-5 μ a meter relay which can be used to operate an alarm. The voltage developed across the meter is also available as a recorder output. The impedance of the meter is 10,000 ohms; therefore full scale (5 μ a) corresponds to a recorder output of 50 mv.

B. Oxygen Detector

1. General

The oxygen detector sensor assembly and bridge circuit are essentially identical with the JP-6 detector, described above. The detectors differ significantly from each other primarily because of the ancillary equipment necessitated by the more complex detection scheme for oxygen. Thus, before contacting the oxygen sensor proper, the gas stream from the fuel tank ullage space must be "processed" to remove excess JP-6 vapor and add isobutane vapor.

2. Condensation of JP-6 Vapors

Removal of JP-6 vapors from the gas stream by condensation was felt to be the most practical method for ensuring against excess fuel concentrations in the oxygen sensor. This could be accomplished by contacting the gas sample with a cold surface. As the availability of refrigerant lines already present in the aircraft cannot be presupposed, the prototype instrument must carry its own means for supplying the necessary low temperatures.

The simplest mechanism by which such a condensor can be cooled is

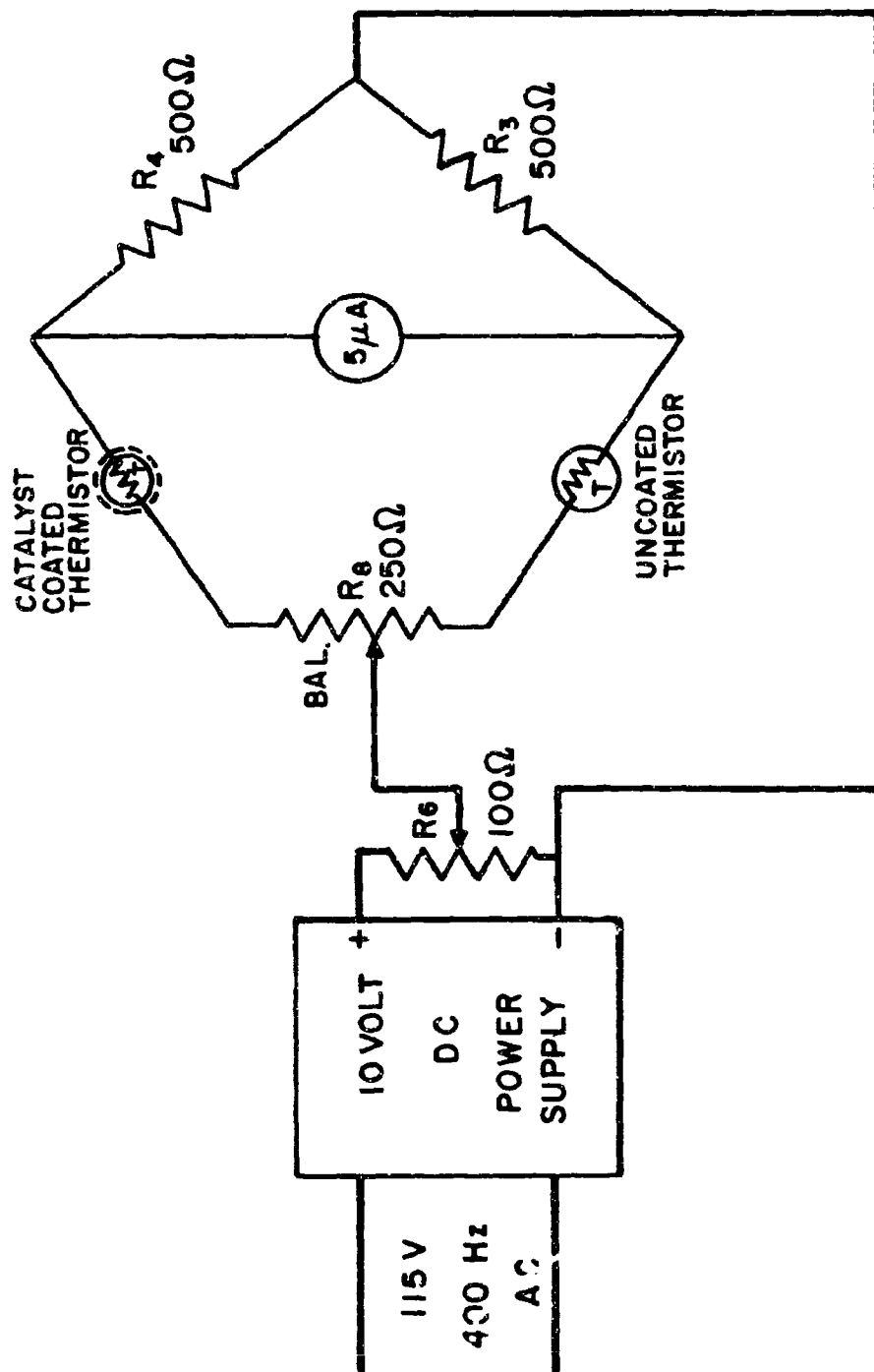


Figure 19. Instrument Bridge

via an evaporative process. In this technique, a liquefied refrigerant under pressure is allowed to evaporate as it expands through a small orifice. The liquid-gas transition is a heat-absorbing process, thus cooling the area in the vicinity of the expansion orifice.

To keep the apparatus as simple as possible, open-cycle operation is preferred. That is, the gaseous refrigerant is not recovered, but is simply vented to the atmosphere. While "wasteful" in terms of refrigerant, operation in this manner eliminates the need for compressors, heat exchangers, etc.

Freon-114 ($\text{CCl}_2\text{F}_2\text{CCl}_2\text{F}_2$) was selected as the refrigerant to be used in this application. It is nonflammable and relatively nontoxic; thus its release in large amounts will present no appreciable hazard.

The design of the condenser assembly is shown in Figure 20. It consists of four concentric tubes, interconnected as shown. The liquid Freon, under pressure, enters the central tube and sprays through the orifice at its lower end into the space between the first and second tubes. It evaporates to a cold gas, which passes into the annular space between the third and fourth tubes, and is then vented. A small thermostat switch, located in the wall of the third tube, controls the Freon flow by opening and closing a solenoid valve on the Freon container. Coolant flow will start when the wall temperature exceeds 90°F , and will stop when it reaches 60°F . It was experimentally determined that the vapor pressure of JP-6 at these temperatures, and hence the JP-6 concentration in the gas stream, was sufficiently low as to not detectably compete with the O_2 isobutane reaction at the catalytic detector.

Gas from the fuel tank ullage space is drawn through the space between the second and third tubes, thus contacting the cold walls, and condensing excess JP-6 vapors. It then passes out of the condenser, after which isobutane is added to the stream.

This assembly is designed to be mounted at the highest point in the fuel tank. The condensed liquid JP-6 is drained out of the condenser by gravity, returning to the bulk fuel. To guard against the fuel in the tank "sloshing" up through the drain hole, and flooding the system, it is fitted with a "snorkel" arrangement, consisting of a float and needle valve. If the liquid level approaches the bottom of the condenser, the float rises and seats the valve, thus closing the drain hole.

3. Gas Flow and Component Placement

Figure 21 depicts the proposed placement of the various components of the oxygen detection system, and the necessary flow paths for the gases involved.

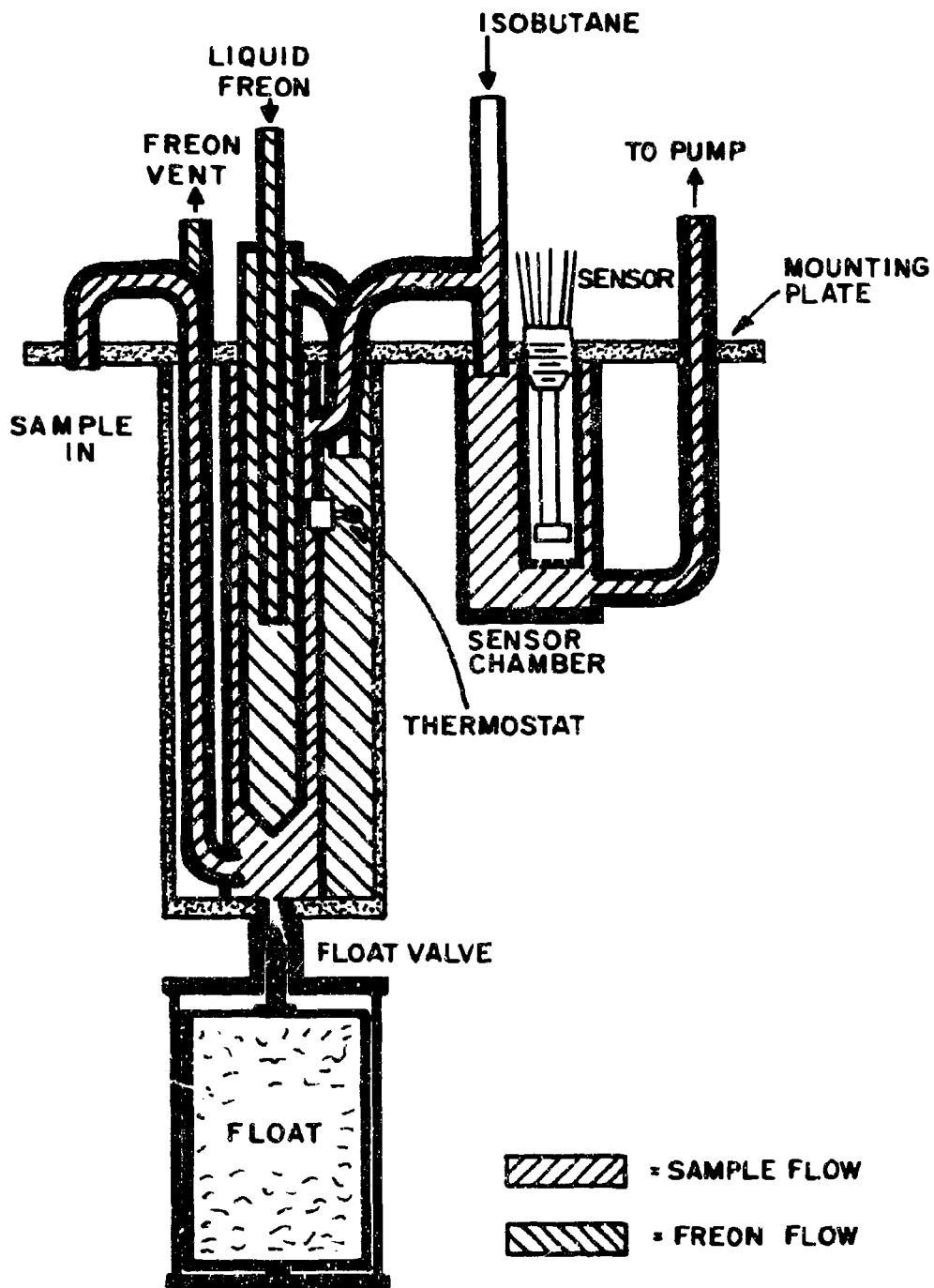


Figure 20. O₂ Detector Assembly

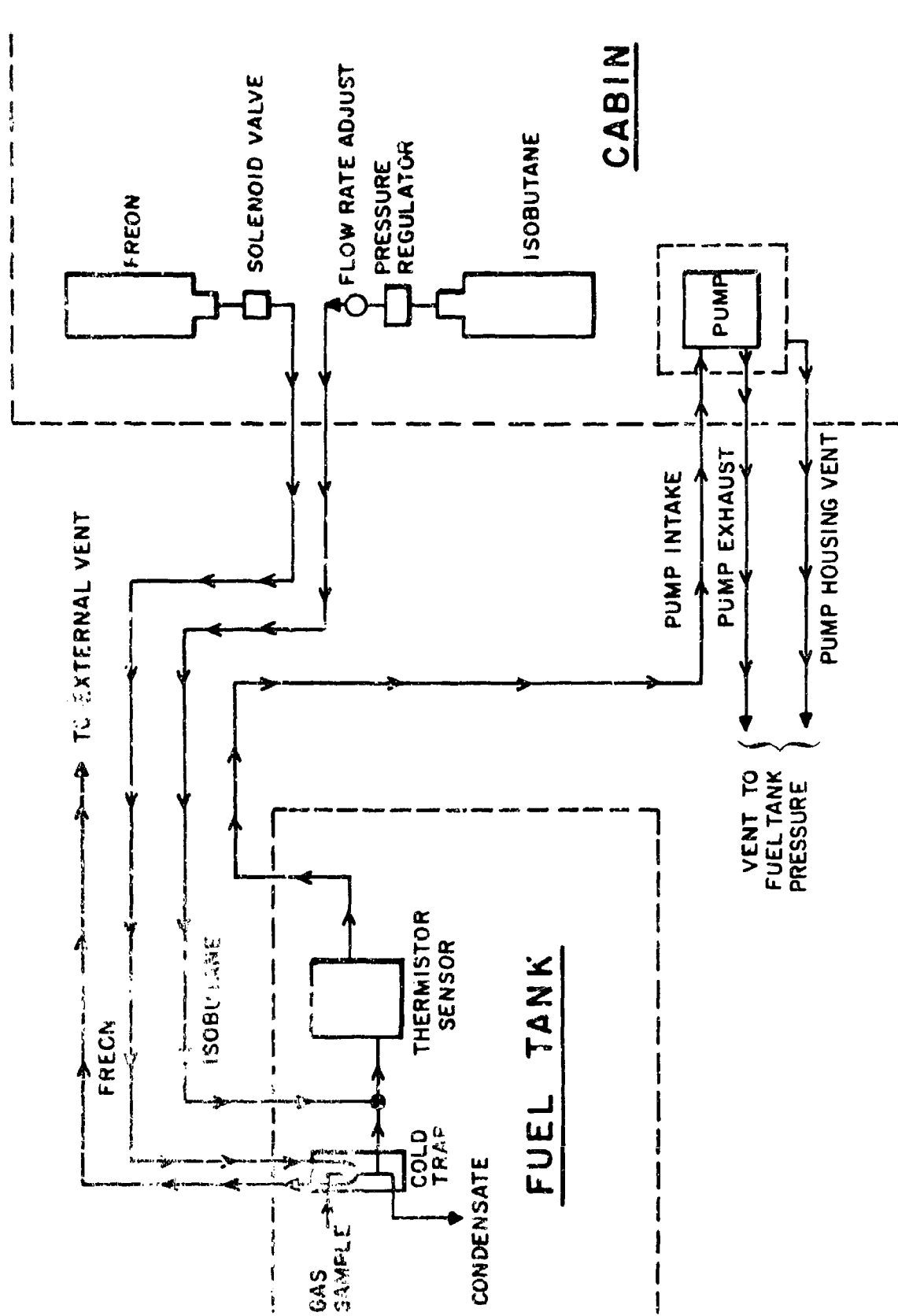


Figure 21. Component Placement and Gas Flows - O₂ Detector

A miniature brushless dc diaphragm pump is used to move the gas through the sensor. The speed of this pump is approximately 3 liters/minute. In order to keep the pressure differential across the pump to a minimum, regardless of the fuel tank pressure, the sampled gas, after being pumped out of the fuel tank, will have to be returned from the pump to an area whose pressure is close to that in the tank. This could be either the fuel tank itself or the outside of the aircraft (if the fuel tank is in pressure equilibrium with the external air).

The maximum operating temperature of the pump is only 90°C. This means that it must be located either in the aircraft cabin or in some other temperature-controlled space. The pump characteristics are such that, if both inlet and outlet are at low pressure, while at the same time atmospheric pressure surrounds the pump housing, the pump motor does not develop enough torque to overcome the pressure on the (collapsed) diaphragm. Therefore, if the pump is located in the cabin area, it must be enclosed in a chamber which is vented to a pressure comparable to that of the gas which it is pumping.

It should be noted that although the line from the pump to the fuel tank may be quite long, this has no bearing on the response time of the instrument. Once the gas enters the sensor chamber (which will be in the fuel tank), the remaining length of line is immaterial.

4. Isobutane Addition

The isobutane is added to the gas stream after it has passed through the condenser, immediately before it passes into the oxygen sensor chamber. A final isobutane concentration in the range 10-15% by volume is desirable if oxygen levels approaching 40% are to be measured, otherwise the high oxygen concentration may cause "quenching." The necessary flow rate of isobutane will be a function of the flow rate of the sample gas stream, and this, in turn, will be dependent on such parameters as the length and diameter of the lines from the pump chamber to the sensor location, the manner in which the pump exhaust and pump chamber are vented, etc. In addition, of course, the dimensions and configuration of the line connecting the isobutane supply with the sensor will affect the isobutane flow rate. As all these factors will depend on the particular physical arrangements which will be made at the time of installation in an aircraft, it was deemed advisable to keep this part of the apparatus as flexible as possible. Therefore, at present, the isobutane flow rate has been left manually adjustable by means of a needle valve located at the cylinder outlet. When installation of the prototype is made, and the appropriate settings found, this valve can readily be replaced by a fixed orifice having the same conductance.

C. Overall Instrument Description

Figures 22 and 23 show the circuitry for a complete instrument. The control box serves as a dual unit, containing the necessary circuitry and controls for operating both a JP-6 detector and an oxygen detector simultaneously. The box contains two identical bridge circuits and readouts which operate, with individually adjustable input voltages, from a common dc power supply. Similarly, there are individual heater controllers for the two sensors.

The JP-6 detector consists of simply a sensor probe, together with the temperature control and bridge circuits in the control box. Additional circuitry and components, however, are necessary for the oxygen detector. When the heater of the oxygen probe is turned on, power is also applied to a 24-vdc supply, located in a separate gas-tight enclosure. This activates the pump, also in the enclosure, which draws the gas sample past the sensor. This power supply also provides the voltage necessary to operate the solenoid valve in the refrigerant line (through the thermostat located in the condenser assembly). A lamp on the control box indicates the state of the solenoid.

The integrity of the alarm system can be ascertained by a "push-to-test" button, which introduces a large bridge imbalance by shunting one of the thermistors. This causes the meter relay to go far up scale, resulting in an alarm signal.

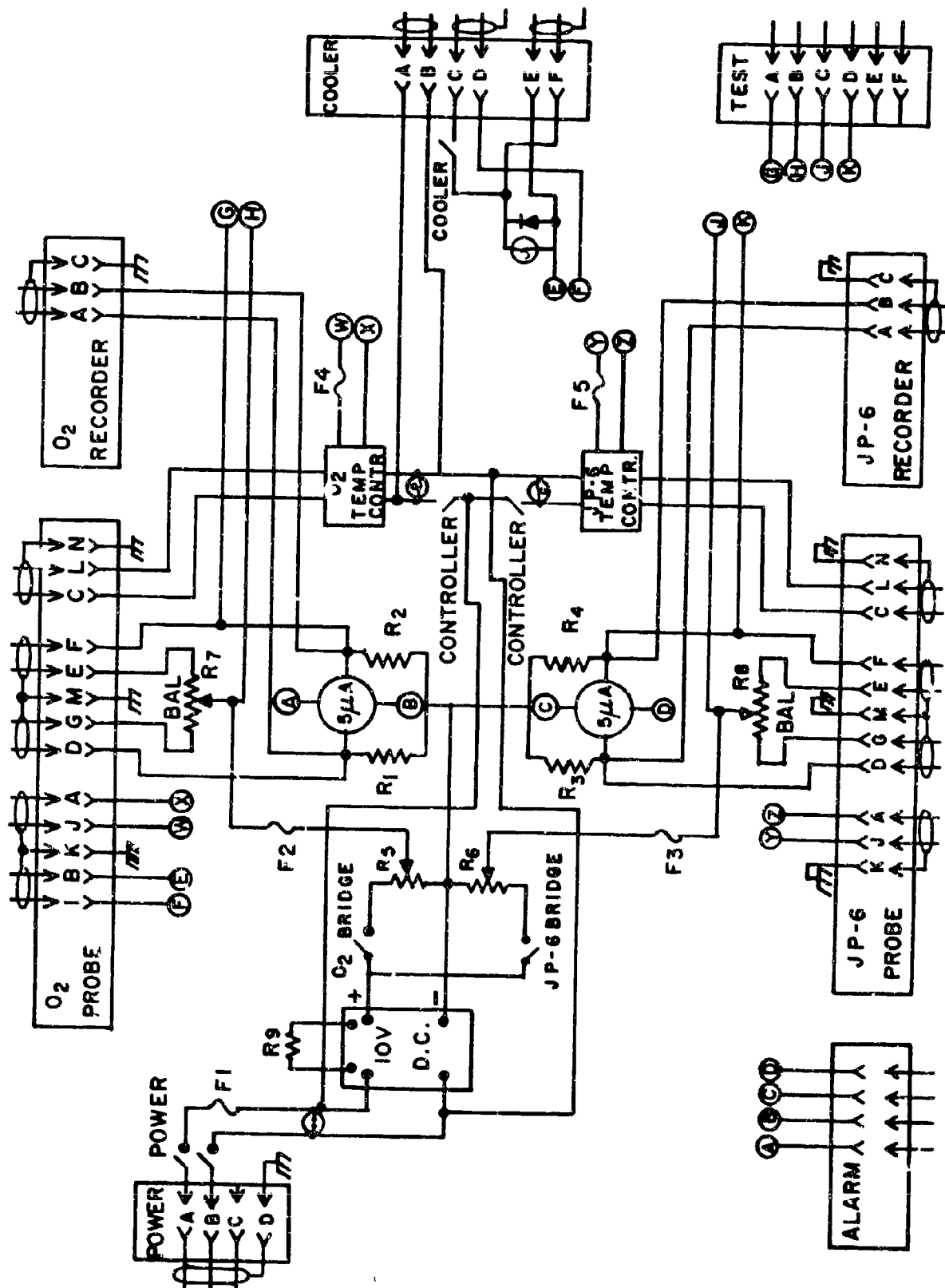


Figure 22. Schematic Control Box

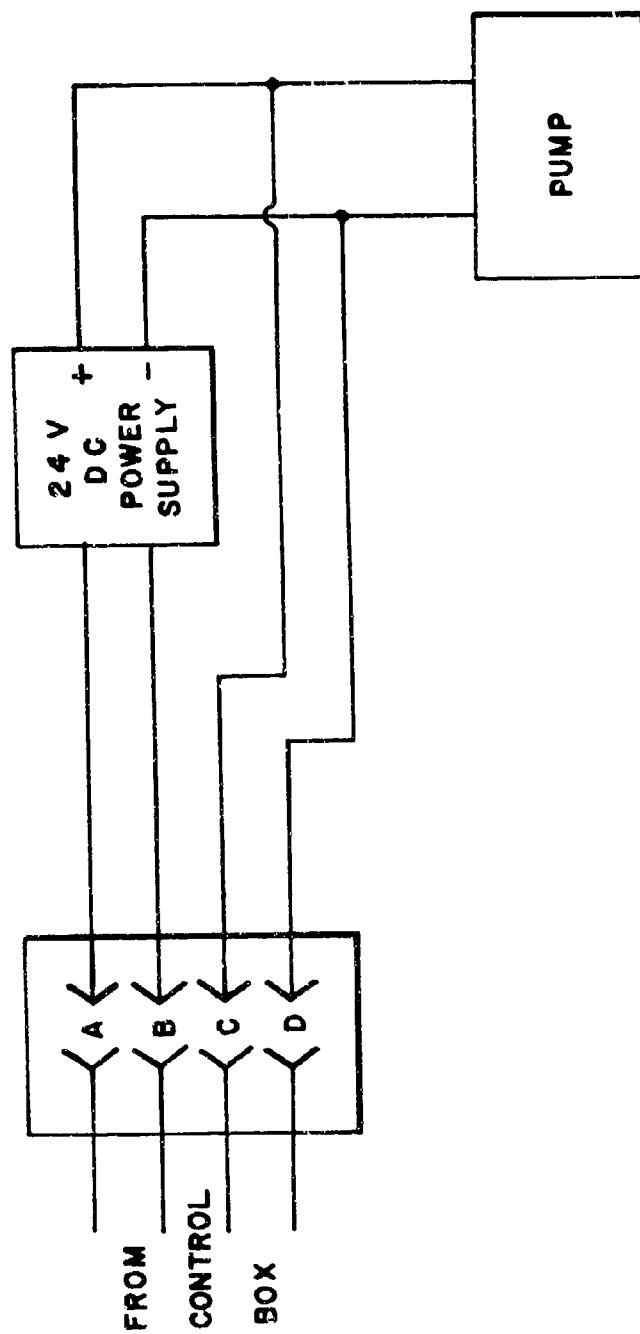


Figure 23. Schematic Pump Circuitry

SECTION IV

SYSTEM TESTS

A. Mechanical

Both the JP-6 sensor probes and the O₂ sensor assemblies (including condensers and float valves) were vibration-tested according to MIL-STD 810-A, Method 514.1, Equipment Class 1, Curve D. The test was performed at an ambient temperature of -65°F. It was not possible to produce an ambient temperature of 650°F surrounding the vibration table; however, while in the -65°F ambient, three of the six sensors were run with their heaters "on", thus producing surface temperatures of 300°C. No evidence of damage to the catalytic coatings was observed upon completion of the vibration tests. The only damage suffered by the units was the partial stripping of the threads on the float valve assemblies of the oxygen sensors, at the point where they screw into the condenser drain holes (see Figure 20). This defect has been corrected by modifying these assemblies so that they are permanently epoxied into place.

B. Temperature Controllers

The temperature controllers were found to maintain the heaters at the appropriate temperature in ambients ranging from -55°C to +300°C. This test was performed by placing the probe in an environmental chamber which could be cycled between these temperature extremes; and observing the thermistor resistances as a function of time. They remained constant.

C. Linearity

Linearity checks were performed on the instruments as part of the process of calibrating them. As expected, it was found that signals were linear, both as a function of JP-6 and oxygen concentrations. The units have been preset to read full scale (5 µa) at 3% JP-6 (by weight) and 20% oxygen, respectively.

D. Freon Cooler

The operation of the Freon cooling system was examined by mounting the O₂ sensor plate on a metal chamber heated to 300°C. With the thermostat and solenoid circuits activated, the system was easily able to maintain the condenser at the set-point temperature (60-90°F) with the Freon "on" less than 10% of the time.

SECTION V

SUMMARY AND RECOMMENDATIONS

Prototype instruments for the detection of JP-6 fuel in engine compartments and oxygen in ullage spaces have been developed, designed, and constructed. Both instruments utilize the heat liberated during catalytic combustion for their detection principle. The JP-6 detector is simple in concept requiring only a detecting probe and associated electronics. The oxygen detector additionally requires a gaseous flow system, a trap to remove JP-6 vapor and the introduction of isobutane as the combustion fuel. These instruments have performed satisfactorily and reliably during the numerous laboratory experiments necessary for development, design, and testing. Throughout the course of this experimentation involving widely varying temperatures, pressures, and compositions of the hydrocarbon-oxygen mixtures, the catalytic probes were never found to be a safety hazard in themselves. Ignition was never observed.

A. Conformance with Target Requirements

1. Temperature Range

The requirement calls for the JP-6 sensing device to operate continuously from -65°F to 650°F , and the oxygen sensing device from -65°F to 550°F . The thermistors presently available, have a high-temperature limit of 300°C (572°F), and this is the temperature at which the heater operates. Therefore, although the oxygen sensor meets the requirement, the JP-6 sensor falls short by about 75°F . Diamond and SiC thermistors have recently been announced and are suitable for use at much higher ambient temperatures. They are, however, either not yet thoroughly evaluated in terms of stability at the high ambient temperatures (SiC) or are not generally available commercially (diamond). Thus, although they are not available for this instrument development program, they could be substituted to achieve the desired operating temperature range.

2. Sensitivity

The sensitivities of the prototype instruments have been shown to be more than adequate in terms of the target requirements (10% of the LEL for JP-6; 0-40% for O_2). The minimum detectable quantities for the prototype instruments are estimated to be less than 2% of the LEL for JP-6, and less than 0.5% oxygen.

3. Response and Recovery Times

The desired response times of the sensing devices are 5 seconds at 10% of the LEL (JP-6), or 0.5% (O_2), and 1 second at the LEL (JP-6)

or 40% (O_2), with recovery times of less than 30 seconds. The response and recovery times of the present sensors are independent of concentration, and are less than 1 second.

The target response time of the complete system, including electronics, is no more than 1 second longer than that for the sensing device. With the recorder output, this requirement is easily met. As has been noted above, these instruments were designed to have maximum flexibility and therefore also have panel meter readouts which contain meter relays required to activate an alarm system. The meters have a relatively high impedance (10,000 ohms) largely because of their associated meter relays whereas the bridge impedance is only about 500 ohms. This mismatch results in a relatively slow system response time (about 5 seconds) when either the meter or alarm readout is used, but when the output signal is fed to a recorder the system response time will be only on the order of milliseconds longer than the sensor response time.

At the time of preparation of this report, it is planned to install the electronics in the instrument bay of an aircraft and to feed only the alarm signal to the cockpit. It is expected that the output will also be recorded. With this mode of installation, the readout meters become superfluous. They can be eliminated and the meter relays, with their inherently slow response, can be replaced by fast acting level sensors which monitor the voltage drop across a sensing resistor located across the bridge circuit. These sensors can be self-canceling, thereby eliminating the interrupter presently required by the meter relays. The net result would be a simpler circuit and an alarm system which would respond well within the desired response time.

4. Selectivity

The instruments readily meet the target requirements of being insensitive to vapors other than the desired species. The nature of the technique, of course, dictates that only those gases which will participate in a catalytic exothermic reaction will be detected, and it is just these gases which can constitute an explosive hazard.

5. Exposure to Liquid Fuel

A specific requirement for the oxygen sensor is that it not be adversely affected by exposure to or submersion in liquid fuel. In view of the relative ease with which catalyst coating can be "washed off" it was necessary to ensure against liquid fuel entering the sensor chamber. This was done by means of the float valve device described above. This valve will function properly only when in a relatively vertical orientation with respect to the liquid fuel surface. It is expected to seat whenever the aircraft attitude alters from the vertical and the sensing chamber is in danger of being flooded. However, only flight experience will demonstrate whether this

seating occurs rapidly enough to prevent flooding of the sensor chamber.

6. Other Requirements

As with all aircraft systems, a prime requirement is that of minimum size, weight, and power consumption. The prototype instruments have the following specifications:

| | |
|--------------------------------------|----------------------------|
| Size - Control Box | 12" x 10-1/2" x 9-1/4" |
| JP-6 Probe | - 4-1/2" x 1-1/2" diam |
| O ₂ Probe Assembly | - 3" x 6" x 9-1/2" |
| O ₂ Detector Pump Housing | - 5-3/4" x 7-1/2" x 5-3/4" |

In addition, the O₂ detector requires 2 gas cylinders (isobutane and Freon), plus associated plumbing. The size of the cylinders will depend on the desired time interval between replacement.

| | |
|--------------------------------------|---------------|
| Weight - Control Box | - 10-1/2 lbs. |
| JP-6 Probe | - 1/4 lb. |
| O ₂ Probe Assembly | - 2 lbs. |
| O ₂ Detector Pump Housing | - 10 lbs. |

Again, the weight of the necessary gas cylinders must be added to the O₂ detector total.

| | |
|-----------------------------------|----------------|
| Approximate Power - JP-6 Detector | - 25 watts max |
| O ₂ Detector | - 31 watts max |

The prototype instruments fulfill the target requirements for continuous operation, built-in system integrity test capability, and having both set-point alarm (self-canceling) and continuous recording capability.

B. Recommendations

There are several areas in which it is believed that the prototype systems may be upgraded:

1. Thermistors should soon be available which will be able to operate stably at temperatures much higher than 300°C. This will allow the JP-6 sensor to fulfill the 1500°F requirement, and to operate with other hydrocarbon fuels, at even higher temperatures.

2. As discussed above, because of installation in the instrument bay, the meter relay should be replaced by fast acting level sensors, thereby

significantly improving the system response time.

3. A 28-vdc power supply is provided with the instrument to provide power for the pump and solenoid used in the O_2 detection system. Another 10-vdc source supplies the bridge voltage. Since a 28-vdc source is available in the aircraft where the flight tests will be performed, the instrument power supplies can be eliminated.

4. Because of the mode of installation and the elimination of the power supply, the electronic circuitry can be reduced in size and weight by a factor of about 3 or 4. It can be almost totally encapsulated thus improving the shock and vibration resistance. Numerous circuit items such as fuses, switches, pilot lights, etc., were used in the prototype for increased flexibility and can be eliminated.

5. The oxygen detection system is complex even though it operated reliably and well in laboratory tests. Simplification in the oxygen detection system is possible if the aircraft cooling system is used to cool the trap in place of the separate Freon system furnished. This possibility depends upon the characteristics of the particular aircraft in which the system is installed.

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APPENDIX

Two other techniques for sensing hazardous vapors were also briefly evaluated during this program. These evaluations are described below.

A. Kryptonates®

1. Operating Principle

The applicability of Kryptonates for the detection of gaseous species has been amply described and reported in the literature.¹⁻³ These solid materials contain the inert radioisotope krypton-85. The solid radioactive source will release gaseous krypton-85 if the structure of the surface is altered by any physical or chemical means. A solid Kryptonate, attacked by a gaseous reacting species will release gaseous krypton-85 at a rate proportional to the rate of the reaction. The rate of release of the gaseous krypton-85 is a measure of the concentration of the attacking gas.

The Kryptonate technique has the capability to selectively detect hydrocarbons and oxygen. Hydrocarbon vapors can be quantitatively determined in the presence of oxygen using a selective Kryptonate sensor. Similarly, oxygen can be determined in the presence of hydrocarbons using a Kryptonate sensor that will react only to oxygen.

One form of a Kryptonate gas detection system involves a sensor cell containing the Kryptonate in powder form, which is a specific reactant for the desired species, a radiation counting chamber, and a small gas sampling pump. The ambient atmosphere is drawn through the sensor cell where reaction occurs; gaseous krypton-85 is released and detected in the counting chamber.

2. Investigation and Results

Under Contract AF33(615)-2477 with Wright-Patterson Air Force Base, an evaluation of various techniques for the detection of hydrogen and hydrocarbons aboard advanced flight vehicles was conducted. It was shown⁴ that homogeneous platinum dioxide Kryptonate, i. e., platinum dioxide with krypton-85 distributed throughout each particle of the material, could detect concentrations of JP-6 fuel in air as low as 0.01 percent by volume (1/60 of the lower explosive limit), at ambient temperatures from below 0°F to 750°F.

Since the detection of JP-6 with platinum dioxide Kryptonate had been evaluated already in some detail, only limited experimentation was conducted during the present program in order to verify prior results.

The major effort in the evaluation of the Kryptonate technique was concerned with the detection of oxygen. Under a program sponsored by the Jet Propulsion Laboratory, an oxygen detector based on the Kryptonate technique was developed by Panametrics.⁵ This detector was developed to ultimately have the capability of detecting oxygen in the Martian atmosphere. The optimum material in terms of sensitivity and response was found to be copper Kryptonate. The final model developed was based on direct source counting, utilizing a foil of copper Kryptonate. The rate of loss of krypton-85 from the sample served as a measure of the oxygen concentration. However, this system was not continuous. Since the present program requires continuous monitoring over a large range of oxygen concentrations, it is apparent that direct source counting would be inapplicable. In order to meet the criterion of continuous monitoring, it is necessary to prepare the Kryptonate sensor in the form of a powder, and utilize an effluent counting system as discussed briefly above, and more extensively in prior reports.^{3,4}

An investigation was conducted to determine if copper could be prepared as a homogeneous Kryptonate powder and to determine if it would release activity at a constant rate with constant oxygen concentration and operating temperature. The results of this investigation were not satisfactory. Although high specific activity, as well as homogeneity of the copper Kryptonate powder were attained, continuous release on reaction with oxygen was not realized. Copper powder Kryptonate was operated at varying temperatures from 200°F to 800°F with varying concentrations of oxygen passing through the sensor cell. Initial responses and sensitivities were excellent. However, after a few minutes operation, signals decreased rapidly. Subsequent analysis indicated that the decreasing signals were the result of a protective oxide layer being formed on the surface of the copper. The melting point of cuprous oxide is 2250°F. This oxide decomposes to the metal at 3260°F. Hence, at reasonable operating temperatures the buildup of such an oxide layer retards further oxidation, and causes the release rate of krypton-85 to decrease even though the concentration of oxygen remains constant.

Thus, it became apparent that copper or other materials which form a protective oxide layer on oxidation, i. e., aluminum, zinc, etc., would not be suitable for continuous oxygen monitoring. Materials which will meet this criterion are those which form volatile oxides or those which form a "flaky" oxide. Such oxide formation would allow oxygen to react at a constant rate, and would not impede the release of gaseous krypton-85.

Two materials which are known to form volatile oxides are carbon and boron. These elements were prepared as powdered Kryptonates and investigated. Although reproducible effluent release of gaseous krypton-85 was observed for constant oxygen and temperature conditions, the temperatures required for sufficient reaction to occur were very high, and were not compatible for usage aboard an aircraft. It was found that in order to measure oxygen in the stipulated concentration range of 0-40% by volume, the

operating temperatures required for both materials were in the 1400°F to 1800°F range. Such high operating temperatures would obviously present a serious ignition hazard.

A more likely candidate material appears to be osmium Kryptonate. Osmium is a fairly hard metal with a melting point of 4900°F. Osmium (and ruthenium) alone among the platinum metals shows a readiness to combine with oxygen. Osmium will react with oxygen directly at 392°F to form the oxide, osmium tetroxide, OsO_4 .⁶ This oxide is volatile at 214°F and hence, at the formation temperature, osmium tetroxide would be continuously vaporized, leaving a clean metal osmium surface for further unimpeded reaction with oxygen.

Because of limited time (two to four weeks are required to prepare homogeneous Kryptonate samples) and funds (osmium costs approximately \$500/ounce) consideration of an osmium Kryptonate oxygen detector was temporarily suspended.

3. Discussion

The feasibility of a PtO_2 Kryptonate detector for JP-6 seems well established. However, at the time when a decision had to be made as to the detection systems to be used in the prototype instruments, no data was available as to the ultimate feasibility of an osmium Kryptonate oxygen detector. Therefore, in view of the desirability of using a single detection principle for both JP-6 and oxygen, Kryptonate systems did not appear as favorable as the thermistor detectors described in the body of this report. In addition, at the time in question it appeared that the thermistor detectors, both for JP-6 and oxygen, would be capable of operation as simple probes, without extensive "plumbing" connections. Kryptonate sensors, on the other hand, would of necessity involve a pumping system to transport the released Kr-85 to a counting chamber.

The thermistor oxygen sensor has become more complex than originally anticipated, however, and an osmium Kryptonate sensor might ultimately be more attractive. Supplementary funds have been allocated for further evaluation of this technique, and this is currently being performed. The results will be reported at a later date.

B. Aluminum Oxide Hygrometer

1. Operating Principle

The possible use of the aluminum oxide hygrometer, manufactured by Panametrics, Inc., for detection of hydrocarbon fuels has been described in detail in a previous report.⁴ The essence of the technique rests on the measurement of the water vapor formed upon oxidation of the hydrocarbon. This measurement is accomplished by means of an aluminum oxide

hygrometer, a relatively new sensing device which has demonstrated excellent sensitivity, accuracy and rapidity in many similar applications. The sensor can readily measure water vapor concentrations ranging from less than .01 $\mu\text{g H}_2\text{O/liter}$ to greater than 20,000 $\mu\text{g H}_2\text{O/liter}$.

The most obvious manner in which this device could be used to monitor JP-6 in air would be to pass the air, first over a desiccant (to remove any ambient water vapor), thence through a heated catalyst cell (to oxidize the JP-6) and finally into a chamber containing the humidity sensor, where the water vapor formed in the oxidation reaction would be measured.

Alternatively, for monitoring oxygen in a fuel tank, the apparatus would be virtually identical, except that the preliminary chemical reaction would necessarily be a quantitative conversion of the oxygen to water vapor, either by reaction with fuel vapors or with a reducing agent present in the cell.

2. Investigation and Results

Previous work had already shown the basic technique to be feasible for detecting JP-6; however, the environmental temperature specification of 650°F could not be met by the commercial form of the hygrometer sensor. The sensor consists of a small strip of aluminum, which is anodized to produce a porous aluminum oxide surface layer. A very thin coating of gold is then evaporated over this structure, resulting in a dielectric "sandwich" consisting of aluminum-aluminum oxide-gold. Ambient water vapor diffuses rapidly through the external gold layer, and interacts with the aluminum oxide matrix; the electrical properties of this "capacitor" are a direct function of the ambient water vapor pressure.

At the time the previous study was performed, the maximum operating temperature of the sensor was limited by the thermal degradation of a polymer used in insulating the electrical lead wires. The objective of the present work has been to investigate whether the sensor could be upgraded to withstand higher temperatures.

Several modified forms of the sensor were studied, including those with an inorganic (silicon monoxide) insulator, and those in which the insulating material had been eliminated completely. These changes resulted in sensors which could survive 650°F without catastrophic failure; however, the sensors did not operate properly at the elevated temperatures, and large shifts in calibration were noted upon subsequent cooling.

3. Discussion

In light of the inability of the aluminum oxide sensor to withstand elevated temperatures, this line of approach was terminated.

REFERENCES

1. D. Chleck, R. Maehl and O. Cucchiara, Krypton-85 as a Universal Tracer, NYO-2757-5, USAEC Contract AT(30-1)-2757 (1964).
2. J. E. Carden, "Preparation, Properties and Uses of Kryptonates in Chemical Analyses," Isotopes and Radiation Technology, Vol. 3, No. 4, (Summer 1966).
3. O. Cucchiara, R. Rex and T. Donaghue, The Development of an Instrument for the Detection of Hazardous Vapors, Contract AF33(615)-1473, AFAPL-TR-65-50 (1965).
4. O. Cucchiara, L. Seiden and T. Donaghue, Investigation of Hazardous Vapor Detection for Advanced Flight Vehicles, Contract AF33(615)-2477, AFAPL-TR-66-71 (1966).
5. D. Chleck and O. Cucchiara, "Radioactive Kryptonates-III. Applications. The Measurement of Oxygen in the Martian Atmosphere," Int. J. Appl. Rad. Isotopes, Vol. 14, 599-610 (1963).
6. F. A. Cotton and G. Wilkensen, Advanced Inorganic Chemistry, Interscience Publishers (1962).

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| 13. ABSTRACT Wright-Patterson Air Force Base, Ohio A program was conducted to evaluate, develop, and construct instrumentation for the detection of hazardous vapors aboard advanced aircraft. Prototype detection systems were constructed both for monitoring JP-6 fuel vapor in aircraft compartments and for monitoring oxygen in the ullage space of fuel tanks. These systems will be further evaluated in flight tests. Detection of both species is accomplished by the use of a catalyst-coated thermistor sensor. Catalytic oxidation occurring at the catalyst surface liberates heat, which is sensed by the thermistor. The JP-6 sensor consists of a simple probe which can be mounted directly in the space to be monitored. No sampling system is required. The oxygen sensor is more complicated, necessitating flow connections to an external pump and gas supplies. The instruments developed meet almost all of the desired goals. In a few instances, flexibility for installation in a variety of situations and locations was retained at the sacrifice of some performance characteristics. Methods for achieving desired goals in specific installations and operating modes are indicated and are relatively simple. | | |

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